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FINAL REPORT

**PROCESSING & PROPERTIES OF SILICON CARBIDE
REINFORCED REACTION BONDED SILICON NITRIDE
COMPOSITES**

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13. ABSTRACT (Maximum 200 words) This research has shown that deficiencies associated with porosity in brittle materials are not intrinsic. By distributing residual porosity in ultrafine pores and avoiding larger microstructural defects, 75% dense reaction bonded silicon nitride (RBSN) samples have exhibited strengths up to 870 MPa. Porosity significantly improves both specific strength (up to 0.36 MPa/(kg/m ³)) by reducing the density, and strain to failure (~0.3%) by reducing the elastic modulus. Use of high purity, small Si powders permitted nitriding schedules to be reduced in severity to combinations like one hour at 1150°C or ten minutes at 1250°C, or in one hour at 1050°C with prerenucleation. These schedules permitted SiC reinforcements to be incorporated into the RBSN matrix without adverse chemical reactions. Silicon carbide particulate composites exhibited improved fracture toughnesses and evidence of R-Curve behavior. Composites made with SiC(w) reinforcements did not exhibit an increased toughness even though matrix-to-whisker bonding fulfilled required criteria because the whiskers contained excessive microstructural and morphological defects. The fine pore structure and the high purity combined to give oxidation rates at 1000 and 1400°C that are 10-20 times less than is observed either with high quality RBSN or fully dense hot pressed Si ₃ N ₄ . Formation of exceptionally thin protective SiO ₂ layers on the high purity RBSN eliminated the usual loss in strength. Extremely small dimensional changes were demonstrated; the shrinkage from the die dimensions to the nitrided part was generally less than 0.25%, and was 0.1 ± 0.05% for mixtures of 88% Si and 12% SiC powders. This research has shown the potential that porous, reaction formed ceramics, like RBSN, have for even the most demanding applications.					
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SUMMARY

Research at MIT and U Mass has shown that characteristic deficiencies generally associated with porosity in brittle materials are not intrinsic, and that many potentially advantageous properties can be realized through slightly modified processing techniques. Based on these results, it is evident that reaction formed ceramics will be able to compete favorably with conventional, fully dense ceramics in many applications demanding maximum properties. Using reaction bonded silicon nitride (RBSN) synthesized from SiH_4 derived Si powder, many longstanding problems with RBSN have been resolved.

Without using property degrading nitriding accelerators like CoO , NiO , FeO , etc., nitriding schedules have been reduced in severity from temperatures which generally exceed the melting point of Si and from times of up to several hundreds of hours to combinations like one hour at 1150°C or ten minutes at 1250°C . With prenucleation, parts made from the high purity Si powders can be completely nitrided in one hour at 1050°C . These reduced schedules and high purities permit reinforcements, such as SiC, to be incorporated without chemical attack and retention of properties to previously inaccessible temperature levels.

By distributing residual porosity in ultrafine pores and avoiding formation of larger microstructural defects, strengths of 75% dense RBSN samples have reached 870 MPa, levels that previously have only been achieved with fully dense Si_3N_4 samples having much higher fracture toughnesses. Rather than being damaging, the porosity in the RBSN improves specific strength (up to $0.36 \text{ MPa}/(\text{kg}/\text{m}^3)$) by reducing the density, and improves strain to failure ($\sim 0.3\%$) by reducing the elastic modulus.

Particulate (p) and whisker (w) based composites were also made successfully with SiC(p) and SiC(w) reinforcements. Fracture toughness increased by a factor of about 1.4 to 1.6 for the case of reinforcement by $15 \mu\text{m}$ size SiC particles, and by a factor of about 1.9 for the $50 \mu\text{m}$ size SiC particle reinforcement. Also, reinforcement by $15 \mu\text{m}$ size SiC particles showed evidence of R-Curve behavior when the SiC volume fraction was sufficiently high (about 38 vol%). Composites made with SiC(w) reinforcements did not exhibit an increased toughness even though matrix to whisker bonding fulfilled desired criteria because the whiskers contained excessive microstructural and morphological defects.

The fine pore structure, responsible for the high strengths, and the high purity, responsible for the enhanced nitriding kinetics, combined to give superior oxidation resistance. At 1000 and 1400°C oxidation rates were 10-20 times less than is observed either with high quality RBSN or fully dense hot pressed Si_3N_4 at the same temperature levels. Rapid formation of exceptionally thin protective layers on the high purity RBSN eliminated the usually observed loss in strength that results largely from cracks which form in the thick SiO_2 films during cooling, and which then propagate into the Si_3N_4 substrate.

Extremely small dimensional changes were also demonstrated. With unfilled Si, the shrinkage from the die dimensions to the nitrided part was generally less than 0.25% without cold isostatic pressing (CIP'ing) and approximately 2.5% with a CIP'ing step; standard deviations were a few tenths of a percent in both cases. Filled RBSN samples allow even tighter tolerances to be maintained. For parts made from a mixture of 88% Si and 12% SiC powders, the total dimensional change was $0.1 \pm 0.05\%$. (A 1-inch die would produce a part that is 0.999 ± 0.0005 inches.)

This research has shown the potential that porous, reaction formed ceramics, like RBSN, have for even the most demanding applications. It has also shown that important issues remain.

Although trends have been identified, the underlying basis for the variation in fracture toughnesses exhibited by the unreinforced, porous matrices remains largely undefined. Extensive and careful characterizations of batches of RBSN exhibiting high and low toughness values revealed differences that are consistent with the toughness levels. The lower toughness material contained larger pores, smaller grain sizes and lower levels of lattice strain than the tougher material. There is evidence that these differences are traceable to the characteristics of the starting Si powders that were employed. Until models for the mechanical properties of intermediate density brittle materials are developed, optimization of microstructural features must be conducted through empirical manipulation of process variables.

Fabrication of parts with practical shapes and dimensions will require binders and solvents. Research to date has shown that the nitridation kinetics are extremely sensitive to the surface chemistry of the high purity Si powders. This research has also shown that while simple hydrocarbons like polyethylene and polystyrene delay the onset of the nitriding reaction they do not inhibit it once it begins. The interaction between surface chemistry, nitriding atmosphere, exposure history and nucleation and growth kinetics will require extensive study before they are understood. Fortunately, these studies can be initiated with solvent and polymer systems which have a high probability of meeting all requirements.

I. INTRODUCTION AND STATEMENT OF PROBLEM

Reaction formed ceramic materials have not approached potential levels of utilization because of historically poor properties and the lack of familiarity by potential users. Research with reaction bonded silicon nitride (RBSN) has shown that reduced processing temperatures and times, high purities, net-shape fabrication, and improved properties can be achieved simultaneously with this class of materials if they are processed carefully by rather conventional techniques.¹⁻⁵ Distinct from conventional high performance ceramics, reaction formed ceramics typically contain relatively high levels of residual porosity. As is true of conventional ceramics, superior properties are feasible with porous ceramics only if the microstructural characteristics of all final phases are precisely controlled; the major difference for the porous ceramics is that the pore structure must be as carefully controlled as is required for the solid phases in a high quality conventional ceramic material.

RBSN is the most widely studied reaction formed ceramic. Processing and property issues encountered with RBSN are typical of many other reaction formed ceramics. Currently, other vapor-phase methods such as chemical vapor infiltration (CVI), and a variety of liquid-phase methods such as reaction bonded silicon carbide (RBSC), various polymer derived ceramics, and the Lanxide™ process are also receiving increased attention. The relatively low processing temperatures, the absence of densification aids that degrade high-temperature mechanical properties, and the absence of shrinkage during fabrication make these processes particularly attractive for the fabrication of ceramic matrix composites. In general, three major problems have been encountered with these reaction formed materials:

1. Residual porosity that is usually present can lead to poor mechanical properties and poor oxidation resistance.
2. Unreacted material is commonly found in materials formed by the liquid-phase processes (e.g., Si in RBSC or Al in Lanxide™ composites), and can also occur in some vapor-phase synthesis routes (e.g., Si in RBSN). In general, this residual phase degrades the properties of the material; residuals are particularly damaging to electrical, optical and elevated temperature mechanical properties.
3. Severe processing conditions are often necessary. In conventional RBSN, complete conversion of the Si typically requires high temperatures and long nitriding times that result in the loss of microstructural control. Most CVI processes require extremely long processing times, and most liquid-phase processes require molten metals that can create handling and contamination problems.

Each of these critical issues has been addressed with high purity RBSN monoliths and composites in research mainly sponsored by ARO. Results clearly demonstrate resolution of these broad problems in large part by using precisely controlled, high purity Si powders and avoiding critical exposures during processing. Sufficient progress has been made that this RBSN is being explored for radomes on hypersonic missiles by the U.S. Army. This

very demanding application reveals important issues whose resolution will make other applications accessible for reaction formed, porous, brittle materials. As has been true to date, further improvements of critical properties will be accomplished only through continued basic research on the interrelationships between process variables, microstructures and resulting properties.

The levels of property improvements achieved with porous ceramics are so great relative to our past experience that they can be viewed as new materials. Precisely controlled synthesis and processing yields highly perfect microstructures with nano-scale features. Though properties and forming conditions are dramatically improved, final synthesis and processing operations are rather conventional. It is through basic modeling of nucleation and growth kinetics, mass and heat transport, relationships between novel microstructures and properties, and other critical steps that the true potential of these materials will be realized.

II. SUMMARY OF RESEARCH FINDINGS

Developments in ceramic materials have typically achieved improved low temperature mechanical properties at the expense of degraded high temperature performance. This generalization results because flaw populations have been improved and/or reinforcements (fibers and particles) have been incorporated with the use of liquid phase sintering aids that enhance densification, but which preclude properties from reaching intrinsic levels at high temperatures.

Reaction formed ceramics represent an important alternative to conventional ceramics which consolidate by densification mechanisms.⁶ Ceramic materials, like reaction bonded silicon nitride, densify through controlled space filling chemical reactions. Because there is no shrinkage during consolidation, high purities can be maintained since there is no need for the liquid phase sintering aids needed to enhance densification and to relieve shrinkage stresses in the vicinity of dimensionally stable reinforcements. Retention of properties to very high temperatures and net-shape are the principal advantages of reaction formed ceramics. Low and unreliable property levels that result from characteristic porosity were the principal disadvantages at the commencement of this program.

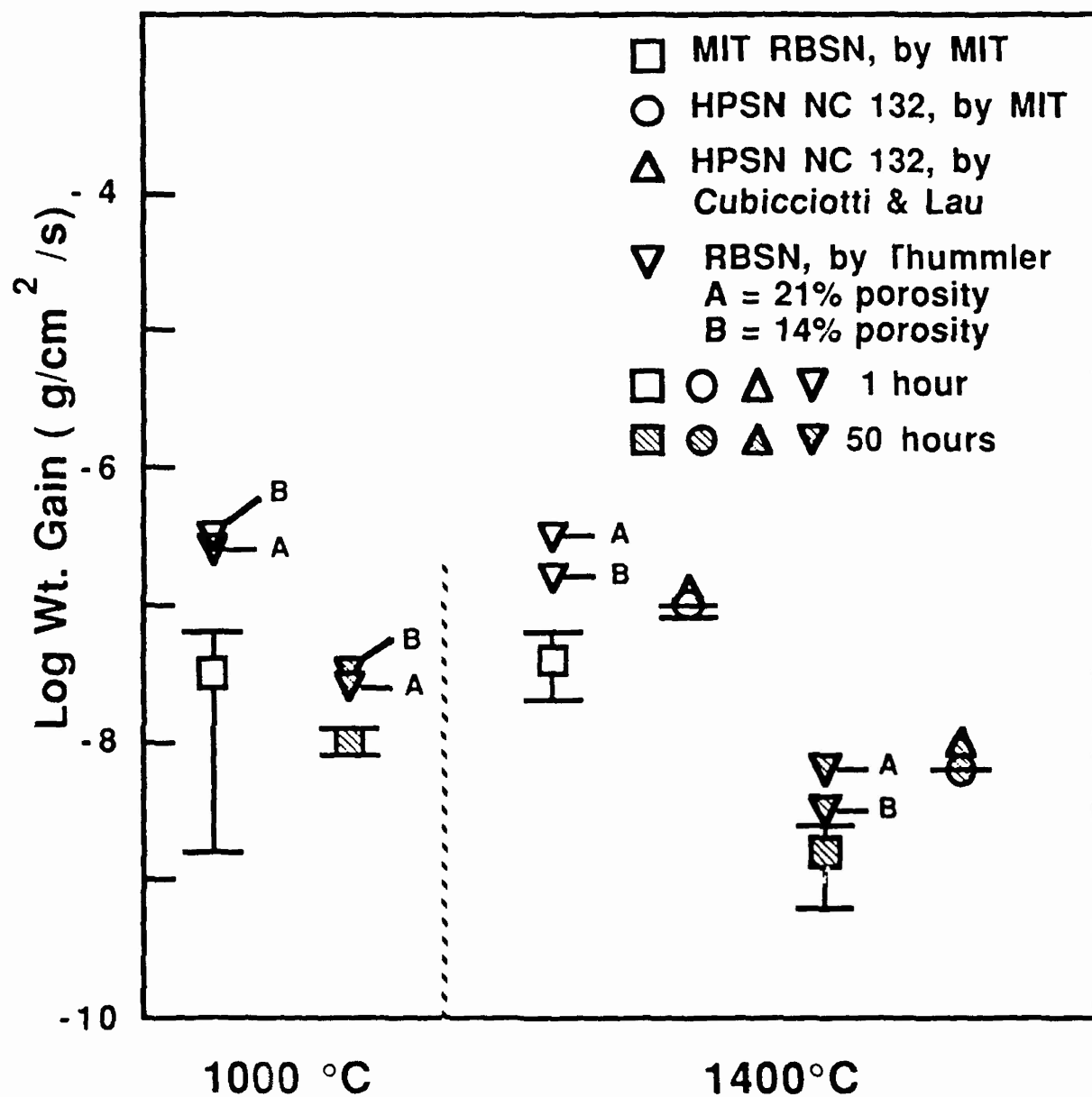
The principal focus of this ARO supported research program has been one of improving the properties of RBSN ceramic materials having relatively high levels of residual porosity. Improved strengths were sought through improved flaw characteristics and fracture toughness. Defects were reduced in concentration and severity through the use of precisely controlled Si powders made from SiH_4 gas⁷⁻⁹ and clean handling procedures. Ceramic matrix composite strategies were pursued to improve fracture toughness since they offered the opportunity for simultaneously improving properties at low and at high temperatures in parts made by a net shape process. Composites based on a RBSN matrix and SiC reinforcements were explored because of their demonstrated technological importance; however, the findings also apply to other materials and to other reaction forming processes. Following Thümmeler's findings,¹⁰ improved oxidation resistance was sought by reducing channel dimensions in the pore structure while maintaining high purity, a strategy that was completely consistent with improving strength. Particularly for the composites, realizing these goals depends critically on reducing the severity of the nitriding process without resorting to additives such as FeO and CoO which accelerate the nitriding kinetics. Precisely controlled exposures to solvents, binders, and atmospheres (ambient and nitriding) were used to retain the extremely fast nucleation and growth kinetics exhibited by the as-synthesized Si powders.

- **Oxidation:** Oxidizing exposures have two principal damaging effects on RBSN. If oxidation occurs within the porous parts, creep rates become comparable to sintered or hot pressed Si_3N_4 , and maximum service temperatures are limited to about 1200°C.¹¹ If the oxide layer becomes too thick when it becomes protective, a polymorphic cristobalite transformation at about 250°C causes cracks originating in the oxide film to

propagate into the RBSN body; these cracks become the strength limiting flaws and result in significantly reduced strengths.¹²

We measured the oxidation kinetics at 1000 and 1400°C, and room temperature strengths after 1 and 50h exposures at these temperatures.¹³ With the high purities and very fine pore structures that characterize these RBSN parts, a thin protective layer formed very quickly. As shown in Figure 1, total weight gains per unit area ($\sim 10^{-9}$ - 10^{-7} g/cm²/s at 1000 and 1400°C) were 10-20 times less than is observed either with high quality RBSN^{10,14} or fully dense hot pressed Si₃N₄ (HPSN)¹⁵ at the same temperature levels. For the cases studied, the exterior protective oxide layers were only 1-2 μ m thick, so widely distributed cracks did not have adequate strain energy to propagate into the RBSN substrates. Unlike other RBSN's and HPSN's subjected to the same oxidizing exposures, Figure 2 shows that these parts did not exhibit any decrease in strength after oxidation. In the less pure Si₃N₄ sample types, pits in the grain boundary junctions and severe cracks in the relatively thick oxide layers became the strength controlling flaws after oxidation.¹² The high purities and fine pore structures in the RBSN, which are generally accessible to reaction formed ceramics, were responsible for these differences. As has been observed in inert atmospheres,¹⁶ formation of protective oxide films should permit virtually complete retention of strengths in oxidizing conditions until dissociation temperatures are reached, ~ 1800 -1825°C.

- **Strength:** Defect-free green microstructures, which are possible with these Si powders, have permitted RBSN strength levels to be increased to levels normally achieved only with the highest quality dense ceramics. We gradually increased the strengths of parts made from these powders, starting from an average level of approximately 350 MPa (50,000 psi) for 60-65% dense RBSN. By using an octanol dispersant for the colloiddally pressed parts, but not employing a cold isostatic pressing (CIP'ing) step, we have produced nominally 75% dense RBSN parts with a mean strength of 590 MPa (85,500 psi) and a maximum of 870 MPa (126,000 psi).⁵ Strength levels were improved primarily by reducing the size of strength limiting flaws to typically 30-50 μ m; flaw populations were improved by eliminating sources of defects (dirt, contaminants, pressing cracks, etc.) and by improving the characteristics of the Si powders (increase mean diameter from 0.05 to 0.25 μ m, reduce aggregates, etc.). The results of mechanical property measurements for sample types studied in this ARO program are summarized in Table 1.5,^{17 19}



Oxidation of Silicon Nitride

Figure 1. Specific oxidation rates for 1 hour and 50 hour exposures to air at 1000 and 1400°C. Samples are: high purity MIT RBSN (references 12 and 13), high quality conventional RBSN (reference 10), and high quality commercial hot pressed Si_3N_4 (reported originally by reference 15 and corroborated by MIT in reference 12).

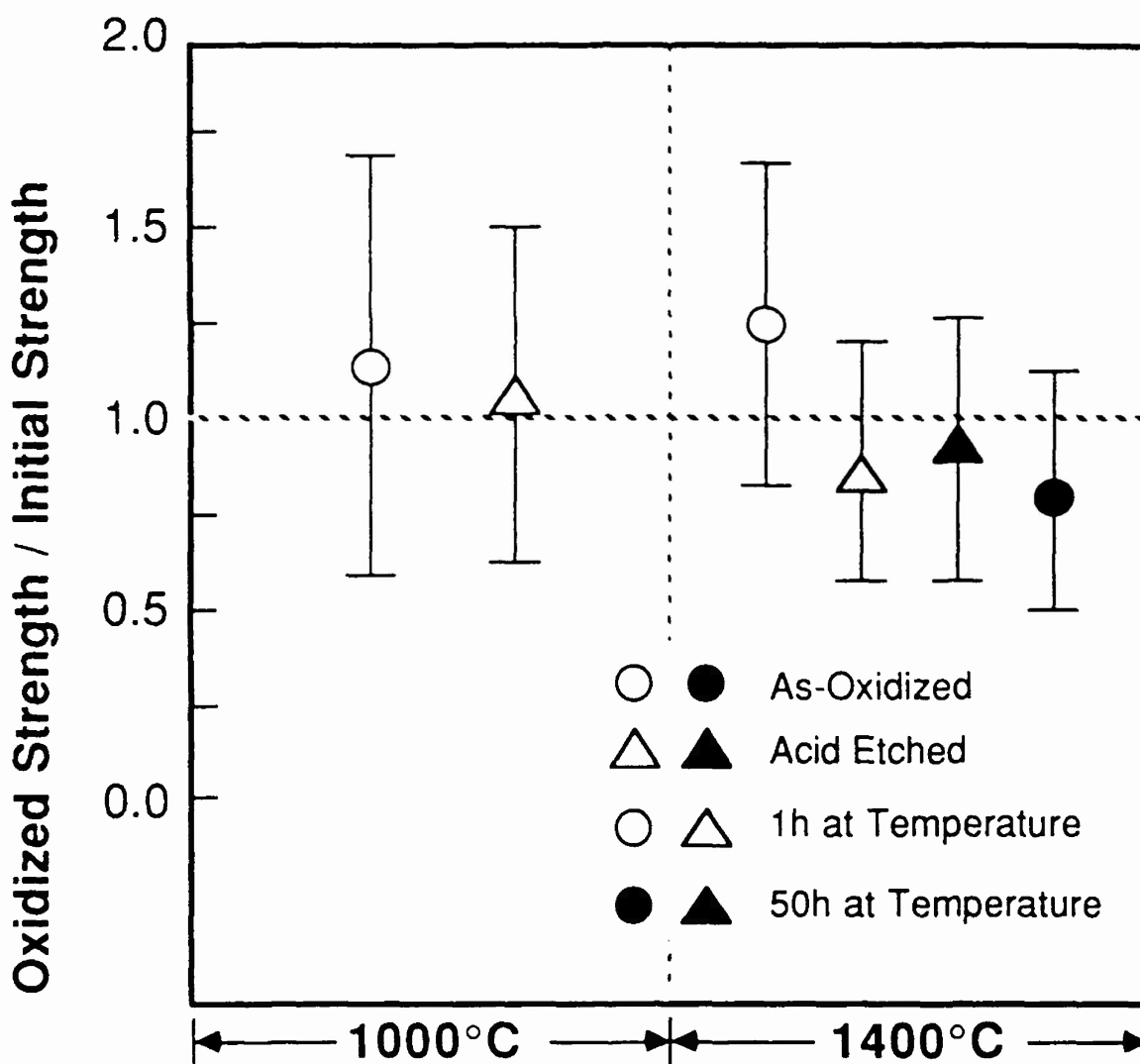


Figure 2. Room temperature strengths of high purity MIT RBSN after oxidation in air for 1 and 50 hours at 1000 and 1400 °C. Samples were tested either as-oxidized or after acid-etching to remove the oxide layer. Strengths were normalized with respect to initial, unoxidized strengths and error bars represent \pm one standard deviation.

Table 1. Summary of mechanical properties measured for RBSN and RBSN/SiC composites

Samples	STRENGTH (MPa)	TOUGHNESS					MIRROR CONSTANT (MPa.m ^{1/2})	HARDNESS (GPa)	MODULUS (GPa) ² (GPa) ³	Fracture Energy (J/m ²) ⁴	FLAW SIZE ^a (μm)
		Indentation Crack Length	Indentation Strength (MPa.m ^{1/2})	Fractography & Site Stress	Toughness						
					Indenation Strength (MPa.m ^{1/2})	Fractography & Site Stress					
RBSN											
Methanol (with CIP)											
Optimization Gp.	441 ± 129	2.4 ± 0.3	--	2.6 ± 0.3	--	8.9 ± 0.5	156 ± 23	--	18 ± 2	--	34 ± 29
Baseline Gp.	401 ± 107	2.3 ± 0.1	--	1.9 ± 0.1	3.8 ± 0.2	9.1 ± 0.4	160 ± 23	--	16 ± 0.2	--	26 ± 19
Oxanol (without CIP)											
High toughness (High K)	592 ± 148	2.5 ± 0.1	--	2.7 ± 0.1	4.6 ± 0.6	10.2 ± 0.4	182 ± 13	189	16 ± 1	18.5	23 ± 11
No.1, Duplicate High K	342 ± 61	2.4 ± 0.4	1.82 ± 0.13	2.00 ± 0.03	3.8 ± 0.2	8.8 ± 0.6	133	166	--	11.5	70 ± 40
No.2, Base Line for 6&13% SiC(w)	--	2.6 ± 0.5	2.13 ± 0.17	--	--	9.2 ± 1.2	139	--	--	--	--
No.3, Base Line for No.6 & 7	445 ± 75	2.5 ± 0.4	1.63 ± 0.15	1.65 ± 0.06	--	9.0 ± 1.1	144	--	--	--	10
No.8, Base Line for No.9	295 ± 138	2.4 ± 0.4	1.63 ± 0.08	1.76 ± 0.04	--	9.2 ± 0.8	147	--	--	--	53
No.10, Base Line for No.11	457 ± 111	2.3 ± 0.3	1.57 ± 0.12	1.81 ± 0.22	--	8.9 ± 1.0	142	--	--	--	19
RBSN Matrix - SiC(p) and SiC(w) Reinforcements											
MIT Synthesized SiC(p)											
12 % Si rich 0.05μm SiC(p)	438 ± 54	2.4 ± 0.1	--	1.7 ± 0.02	3.2 ± 0.1	7.8 ± 0.5	150 ± 10	--	19 ± 1	--	33 ± 10
10 % C rich 0.05μm SiC(p)	517 ± 130	2.4 ± 0.2	--	2.3 ± 0.03	4.1 ± 0.3	9.8 ± 0.7	166 ± 14	--	18 ± 4	--	35 ± 10
20 % C rich 0.05μm SiC(p)	313 ± 66	2.2 ± 0.1	--	2.0 ± 0.1	3.4 ± 0.2	7.4 ± 0.4	115 ± 10	--	21 ± 2	--	29 ± 9
Commercial SiC											
6 % 2μm SiC(w)	307 ± 44 ¹	2.9 ± 0.4	1.93 ± 0.21	--	--	8.6 ± 1.1	172	--	--	--	--
13 % 2μm SiC(w)	347 ± 39 ¹	2.6 ± 0.4	1.87 ± 0.35	--	--	8.9 ± 0.9	143	--	--	--	--
17 % 2μm SiC(p) (No. 6)	437 ± 62	2.4 ± 0.4	1.76 ± 0.12	1.94 ± 0.08	--	10.6 ± 1.2	171	--	--	--	30.50
33 % 2μm SiC(p) (No. 7)	496	2.3 ± 0.3	2.00 ± 0.17	2.07 ± 0.08	--	7.6 ± 0.7	123	--	--	--	30.50
22 % 15μm SiC(p) (No. 9a)	273 ± 32	3.1 ± 0.4	2.46 ± 0.14	--	--	9.2 ± 0.8	147	--	--	--	--
22 % 15μm SiC(p) (No. 9b)	--	3.2 ± 0.4	3.0 ± 0.8	--	--	11.0 ± 1.3	176	--	--	--	--
21 % 50μm SiC(p) (No. 11)	171 ± 6	3.5 ± 0.7	--	3.11 ± 0.42	--	11.4 ± 1.3	182	--	--	--	302

- 1 Strengths measured in 3-point flexure, test measured by ball-on-ring technique
- 2 Modulus defined by Vickers and Knoop hardness measurements
- 3 Modulus determined by acoustic velocity measurements
- 4 Defined as $K^2/2E$ where E is determined from hardness measurements
- 5 Defined as $K^2(1-\nu^2)/2E$ where E is determined by laser pulse measurements

These results show that porosity need not have any detrimental effect on strength, provided it is uniformly distributed in pores whose dimensions are much less than the strength limiting flaws. If made properly, RBSN can exhibit absolute property levels that are near the maximum values exhibited by Si_3N_4 , and can have superior specific strengths (up to $0.36 \text{ MPa}/(\text{kg}/\text{m}^3)$) and strains to failure ($\sim 0.3\%$) because of their low densities and reduced moduli; similar results can be anticipated for other porous, reaction-formed materials.

The unusually high strengths resulted from a combination of the anticipated small flaw size and the relatively high fracture toughnesses exhibited by only certain batches of RBSN samples. Contrary to predictions for this range of porosity, we have found that fracture toughness is not a simple function of density. For instance, for 75% dense RBSN samples made by nominally identical processing histories, but originating from different batches of nominally identical Si powder, we have found that subtle differences in detailed microstructural features cause the K_{IC} to vary from ~ 1.6 to 2.9

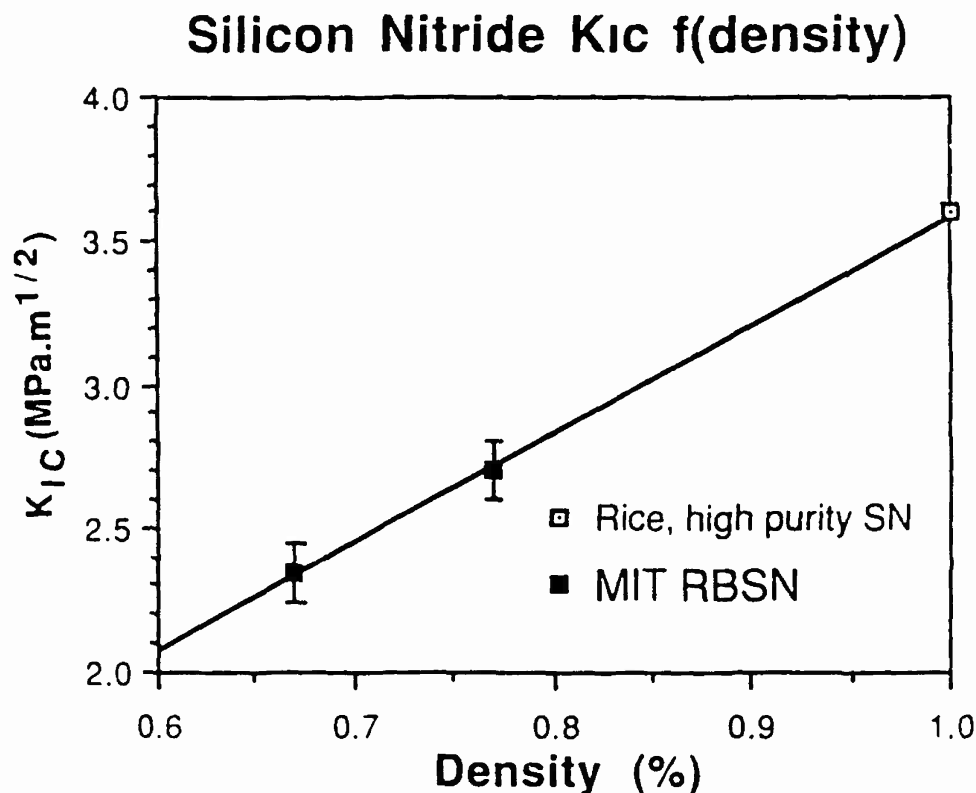


Figure 3. Fracture toughnesses of high purity Si_3N_4 as a function of density. The two porous RBSN data points represent the maximum batch-average values observed for the high purity MIT RBSN at both density levels (references 5 and 17). The fully dense value represents an estimate of an intrinsic value for Si_3N_4 that is free of the effects of glassy grain boundaries (reference 20). These data points suggest porosity has no more than a linear effect on K_{IC} . However, this curve may substantially underestimate accessible toughnesses, since Heinrich observed $5.4 \text{ MPa}\cdot\text{m}^{1/2}$ for 75% dense RBSN.

MPa·m^{1/2}. From the results shown in Figure 3, that are based on maximum observed K_{IC} values for the MIT synthesized RBSN^{5,17} as well as the toughness of fully dense high purity Si₃N₄,²⁰ it is evident that K_{IC} decreases no faster than linearly with porosity and that there is no intrinsic basis for the exponential dependence predicted by popular models. Heinrich's result for RBSN nitrided at 500 atm. N₂ ($K_{IC} = 5.4$ MPa·m^{1/2} for $\rho/\rho_0 = 76\%$)²¹ suggests that the linear relationship given in Figure 3 substantially underestimates fracture toughness levels that are accessible with porous materials.

The other properties summarized in Table 1 have also been considered in detail. With the exception of fracture toughness, their discussion will be omitted since they were not the focus of this research program. Our investigation of factors responsible for the variation in fracture toughness is discussed in the next section.

- **Microstructural Characterization:** Detailed microstructural characterizations of fully nitrided samples were made to identify distinguishing characteristics between high- and low- K_{IC} samples.^{22,23} RBSN samples as well as constituent powders were examined by SEM/FEG, TEM, BET, XRD, and Hg-porosimetry to define microstructural and fractographic characteristics. Though focused on interpreting differences in observed mechanical properties, the results apply equally to the nitriding process which defined the final microstructures. The results for two batches of samples, designated "High Toughness" and "No. 1, Duplicate High K" in Table 1, are summarized in Table 2 as High K and Low K respectively. These specific batches were selected because they represented extremes in K_{IC} values at that time; as shown in Table 1, subsequent RBSN batches exhibited even lower values.

Most of these results are within ranges reported previously for RBSN made from SiH₄-derived Si powders. The specific surface areas confirm that the interiors of the samples are generally open to the exterior surfaces and that the RBSN microstructure retains the small characteristic dimensions of the starting powders. TEM and SEM micrographs (Figure 4) show that the RBSN is characterized by a highly tortuous structure with interconnected, cocontinuous pore and solid phases. In most micrographs, it is almost possible to traverse the figure by following a path through either the pore or solid phase. Pore shapes and sizes vary. With some license, the porosity can be grouped into somewhat irregular larger pores and narrower pore channels. The largest dimension of most pores falls in the range of 20 nm to 250 nm, with an average of approximately 130 nm. Pore channels vary in width within an approximate range of 10 nm to 40 nm. The solid phase appears as an interconnected, high aspect ratio ribbon-like structure that presumably extends in all directions throughout the microstructure. The widths of the solid phase are in the range of 80-400 nm. From these micrographs, it is not possible to conclude whether the solid phase has a cylindrical, strut-like structure, or whether it is more like a cell wall and extends in two dimensions.

Table 2. Summary of characteristics for high and low fracture toughness RBSN

Characteristic	Method	High K	Low K
Bulk Density (%)	Pre-nitrified Si	62	59
	Nitrified	76	75
	Skeletal (He pyc)		~85
Porosity (%)	Bulk	24	25
	Point Count	46.1	41.3
	Closed (< 10 nm, Hg PS)		12.6
	Closed (< 3 nm, Hg PS)		15
Pore size (nm)	SEM	20-250	20-250
Pore channel dia (nm)	SEM/TEM	10-40	10-200
	Hg PS		10-40
Extent Nitrified (%)	XRD	>98	>98
	Weight gain	96.3	96.8
α/β	XRD	4.1	3.0
Surface Area (m ² /g)	BET	2.9	3.3
	Intercept/Point Ct	5.6	6.6
BET Eq. Spherical Diam. (μ m)		0.66	0.56
Grain Size(nm)	TEM	114	76
	XRD*	65.7 \pm 4.3	45.6 \pm 8.1
Lattice distortion (%)	XRD*	0.20 \pm 0.02	0.15 \pm 0.03
Lattice parameter a (nm)	XRD*	0.7760 \pm 0.0004	0.7768 \pm 0.0009
Lattice parameter c (nm)	XRD*	0.5627 \pm 0.0004	0.5635 \pm 0.0008
Strength (MPa)	Ball on Ring	592 \pm 148	342 \pm 61
Toughness (MPa·m ^{1/2})	Fractography	2.7 \pm 0.1	2.0 \pm 0.03
Mirror Constant (MPa·m ^{1/2})	Fractography	4.6 \pm 0.6	3.8 \pm 0.2
Elastic Modulus (GPa)	Sonic Velocity	189	166
Flaw Size (μ m)	Fractography	23 \pm 11	70 \pm 40

* α -Si₃N₄ phase only

Fracture surfaces of lower toughness RBSN revealed clusters of pores arranged in two dimensional arrays that were not evident in the high toughness samples. The widths of these larger than average pores, or channels, range from 100 nm to 200 nm. The apparent lengths of these channels vary from 400 nm to 800 nm in some samples, while in others, the channels appear as a continuous cell-like network that extends over distances > 150 μ m, isolating uniform porosity-level RBSN islands that range in diameter from ~1 to ~10 μ m. In most cases, the channels exhibited intermediate aspect ratios. Examination of low toughness samples with bulk densities ranging from 72.3 to 75.8% revealed that the extent to which the pore networks developed increased with bulk porosity. The low toughness RBSN appears to be distinguished by a relatively large channel defect that has a tendency to form as a continuous network.

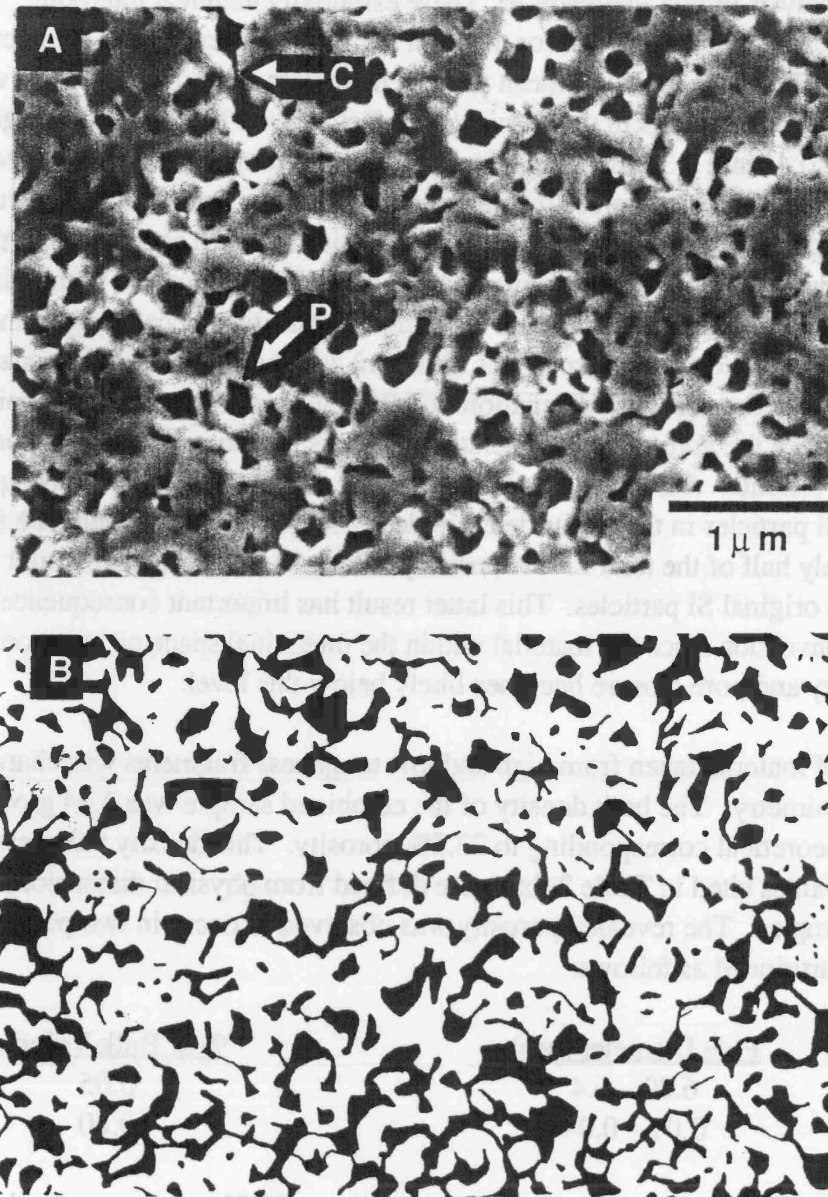


Figure 4. Microstructure of Ar ion polished low toughness RBSN a) as observed by SEM and b) after highlighting porosity for image analysis. The microstructure is typical of both high and low toughness RBSN. Features P and C are examples of irregularly shaped large pores and narrow pore channels, respectively.

The mean spacing between larger pores was determined from highlighted micrographs by manual analysis of line intercepts.²⁴ These essentially identical interpore dimensions are 0.54 and 0.55 μm for the high and low toughness RBSN materials respectively. Using the actual Si mean particle diameters and bulk Si density values, the Si interparticle spacings in the prenitrided pellets for the high and low toughness materials are 0.41 and 0.39 μm respectively.²⁵ The agreement between interpore spacings and the estimated values for mean center-to-center spacings of Si particles in the green parts suggests that the larger pores are relics of the Si particles, and that the reaction product (containing interconnected channels) initially formed within the interstitial regions between the original Si particles. The difference between the mean pore diameter defined from micrographs (130 nm) and the mean Si particle size (300 nm) results from the necessary formation of RBSN within the volumes occupied by the Si particles since the volume of the interstitial space is inadequate to accommodate all of the reaction product. Assuming that the number of pores within the RBSN equals the number of Si particles in the unnitrided sample, these diameter ratios indicate that approximately half of the total RBSN porosity is located within the interstitial space between the original Si particles. This latter result has important consequences for complete conversion since the material within the interstitial space contains only 10 to 15% porosity and pore closure becomes likely below this level.

A mixture of material taken from high and low toughness fragments was characterized by Hg-porosimetry. The bulk density of the combined sample was 2.44 g/cc, or 76.7% of theoretical corresponding to 23.3% porosity. This density value essentially equals the values cited in Table 2 that were defined from physical dimensions of polished samples. The revealed porosity was observed to occur in two pore size ranges that were partitioned as follows:

<u>Pore Diameter (μm)</u>	<u>% of Bulk Volume</u>
6.00 - 6.4	0.05
0.01 - 0.04	10.60

The large pore channels evident in the low toughness RBSN were not revealed by Hg-porosimetry, showing that they are not interconnected with the exterior surfaces through large diameter paths. Also, 12.65% of the bulk volume, over half the total porosity, was not revealed by Hg-porosimetry, indicating that the residual porosity is either accessed through pore channels smaller than 0.01 μm , or it is closed. If interconnected pores are assumed, neither the volume fractions nor the sizes of the pores revealed by Hg-porosimetry are consistent with TEM and SEM microscopy observations unless it is concluded that the pathways to half of the larger pores are defined by extremely narrow (< 10 nm) necks in the pore channels. He-pycnometry measurements of as-nitrided and surface ground samples both indicate skeletal densities are ~85%, indicating that approximately 15% of the RBSN sample volumes, >50% of the total pore volumes, are made up of closed pores. Similar discrepancies in densities

have been observed with high surface area sol-gel materials which were attributed to the effects of adsorbed species.²⁶ The differences between specific surface areas defined by BET and microstructural analysis given in Table 2 could be caused by the existence of pores in the RBSN that closed after cooling and exposure to the ambient.

Although there is considerable evidence of closed porosity in the RBSN, we feel it is extremely unlikely that significant fractions of these samples could have been isolated from the exterior surfaces under nitriding conditions based on the observed nitriding kinetics. If pore closure occurred, it probably happened only after nitridation was completed, possibly during the initial cooling.

Extensive high resolution TEM analysis of very carefully prepared samples will be required. TEM micrographs revealed an ~10 nm thick amorphous layer on the surfaces of the pores and channels which appeared to block occasional channels. In one case, a 135 x 180 nm grain of residual Si was identified. As was expected from proposed models of the nitriding process,^{27,28} the Si grain was surrounded by numerous Si₃N₄ grains and three pores which create the exposed Si surfaces needed for rapid, low temperature nitridation. The fact that no channels were connected to these pores may be responsible for its failure to convert to Si₃N₄. The details of the pore structure will have important consequences for properties as well as nitriding kinetics.

Grain sizes have been defined by X-ray line broadening and from TEM micrographs. The TEM results summarized in Table 2 represent average intercept lengths on the micrographs. Because TEM foil thicknesses are roughly equal to the observed grain sizes, the relationship between intercept length and grain size does not match either of two limiting cases. If the foil was much thinner than the grain size, it would approximate a metallographic section, and the mean grain diameter would equal 3/2 the mean intercept length.²⁹ If the foil was much thicker than the grain size, the observed intercepts would equal the grain diameters. Thus, true grain sizes lie between 1.0 and 1.5 times the values cited in Table 2.

The TEM derived intercept lengths have the same relative values for high and low toughness RBSN sample types as the grain sizes observed by X-ray line broadening in Table 2, but are almost two times larger. Using the factor of 1.5 would increase this discrepancy to a factor of 3. The difference between TEM and X-ray derived grain sizes probably results largely from faults in the grains, since the X-ray technique will yield the diameters of fault-free coherent scattering domains, and TEM intercepts measured the diameters of grains which included faults.

The number of Si₃N₄ nuclei that form on each Si particle is strongly dependent on the size of the resulting Si₃N₄ grains since the diameter is cubed in the calculation. Analyses based on the X-ray defined grain sizes given in Table 2 yields number of nuclei that are up to an order of magnitude higher than the values we have reported

previously²⁸ (5-50, generally ~ 10) which were defined by a different X-ray line broadening technique that did not separate grain size and lattice distortion effects. The TEM micrographs show that the correct dimension for this type of analysis probably should be the TEM derived value. With the factor of 2 to 3 correction in grain sizes, the number of nuclei per particle based on TEM derived sizes are in the same range (4-12) as those defined in reference 28.

The X-ray results reveal distinct differences between the high and low toughness RBSN samples. Based on similar standard deviation values, the grain sizes of the low toughness RBSN are significantly smaller and the lattice distortions are slightly lower than the high toughness material. The higher level of lattice distortion may result directly from the larger grain size since lattice mismatch stresses frequently increase with the characteristic dimension of the reaction product. Preferred growth directions³⁰ probably result in anisotropic stress fields. For all of the samples, the lattice distortion levels are extremely high relative to typical macroscopic strains to failure; nominal internal stress levels are in the range of 175-402 MPa based on a modulus of 175 GPa. Reported relationships between lattice parameters and oxygen content³¹ indicate that the high and low toughness RBSN samples contain between 0.05 and 0.3 weight percent oxygen, and that the lower toughness RBSN had the lower level of oxygen contamination.

Although not fully understood, these results demonstrate the important effects details of the synthesis reaction mechanism and subtle changes in defect structures have on the properties of the reaction formed ceramics through their direct effects on resulting microstructures.

- **Toughening with SiC Fiber and Particulate Reinforcements:** Prior to initiating experiments, alternative toughening mechanisms based on fiber and particulate reinforcements were evaluated in terms of two groups of issues.³² In the first, we assessed their applicability to porous matrices and projected probable levels of toughening. In the second, we considered specific candidate reinforcements, and made quantitative estimates of mechanical properties based on assumed levels of interface bonding, volume fractions, sizes, etc. (see Section below on Development of Fundamental Toughening Models). Reinforcements that were considered for RBSN matrices included SiC and Al₂O₃, as both whiskers and spherical particles.

Bridging with SiC fibers or whiskers provided the best opportunity for significant toughening, with composite (K_c) to matrix (K_m) toughness ratios (K_c/K_m) up to 10 appearing accessible. Through a combination of crack deflection, microcracking and residual stress effects, toughening ratios up to approximately 2 appeared feasible with SiC particles. Toughness ratios up to 3.2 were predicted for 10 μ m diameter Al₂O₃ particles; however, stresses induced by the large difference in thermal expansion

coefficients between Al_2O_3 and RBSN indicated probable bond failure and/or spontaneous fracture of the Al_2O_3 particles.

We concluded that porosity in the matrix phase had little impact on potential toughening beyond its direct effects on the elastic modulus of the matrix, and its strain to failure. Whisker or long fiber reinforcement offered the greatest opportunity for reinforcement, but presented serious processing issues in terms of achieving required fiber architectures and avoiding defects in the matrix and reinforcements. Significant toughening with less difficult processing appeared feasible with the particulate approach. It was decided to simultaneously investigate SiC whisker and particulate reinforcements since they both offered opportunities for significant toughening and because little was known about the SiC-RBSN bond strengths, other than that VLS-SiC whiskers exhibited fairly long pullouts in this high purity RBSN. SiC particulate and fiber reinforcement mechanisms require different bond strengths since weak bonds are sought for fibers and strong bonds are needed for particles having a high thermal expansion coefficient that exceeds that of the matrix.

The variation in toughnesses exhibited by nominally identical RBSN samples made it difficult to interpret the effects that reinforcements had on composite properties. However, using both indentation-fracture and fractography techniques to measure fracture toughness in combination with base-line RBSN samples made from corresponding Si powder batches, it was possible to demonstrate toughening.

Particulate composites were made with 0.2 to 0.3 μm diameter high purity SiC powder synthesized at MIT, and with 15 and 50 μm diameter Acheson derived α -SiC powders. Although the small SiC had only a slightly improving effect, using both 15 and 50 μm diameter SiC particulate reinforcements in the RBSN resulted in a substantially increased fracture toughness.^{19,32} Fracture toughness increased by a factor of about 1.4 to 1.6 for the case of reinforcement by 15 μm size SiC particles, and by a factor of about 1.9 for the 50 μm size SiC particle reinforcement. Also shown in Figure 5, reinforcement by 15 μm size SiC particles showed evidence of R-Curve behavior when the SiC volume fraction was sufficiently high (about 38 vol%).

From direct observations of crack-microstructure interactions, the toughening appeared to be due to crack bridging in the crack wake and due to microcracking of SiC particles in advance of the propagating crack.¹⁹ Illustrating the need for improved theoretical understanding of these materials, the operative toughening mechanisms did not conform to our assumed behavior. For example, matrix cracks were not deflected around the SiC particles, but took a path through the particles themselves as a result of particulate fracture in advance of the matrix crack. Strengths did not improve proportionally with the toughnesses because processing flaws were slightly larger in the mixtures of highly dissimilar particles. From these results, it is evident that

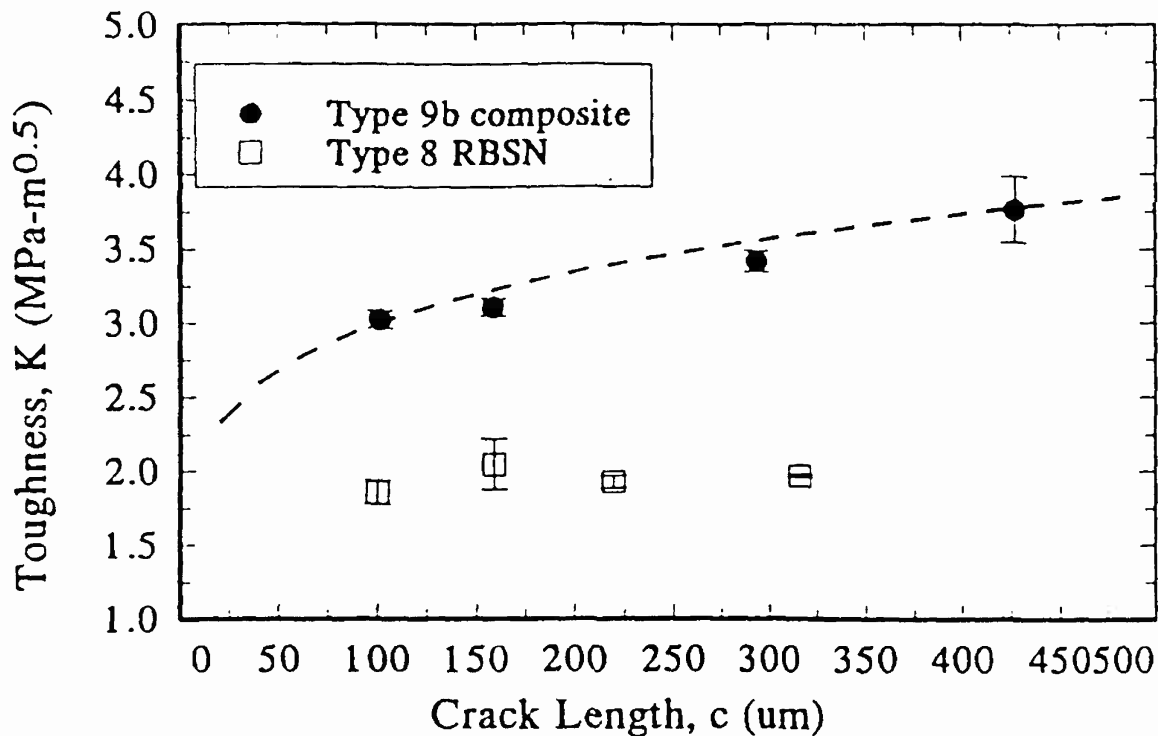


Figure 5. Fracture toughnesses as functions of crack lengths for RBSN baseline and RBSN-SiC(p) composite showing toughening and some R curve behavior.

particulate toughening offers an important opportunity for improving the properties of these intermediate porosity, brittle materials.

Composite samples containing 6 and 13 volume percent Tateho SiC whiskers were made at Rutgers University using their special whisker facilities. These composite samples were not toughened with respect to the baseline RBSN samples.³² Scanning electron microscopy revealed that a significant fraction of the as-received Tateho whiskers did not have the ideal cylindrical shapes needed for toughening by pullout. Fluctuations of the diameters along the lengths of the whiskers gave curved and/or knobbed morphologies. In some cases, sudden changes in diameter created natural stress concentrators. Side growths frequently produced whiskers with "Y" and "L" shapes. Small, stubbular growths were seen both at the ends and along the lengths of the whiskers. End holes indicate hollow cores which are known to exist in a fraction of the Tateho whiskers. A TEM of the composite verified that all of these morphological features were retained during processing.

Fracture surfaces of the whisker reinforced composites did not show signs of significant pullout, although many whiskers and their relics were evident. SiC(w) were observed lying lengthwise on the surfaces and complementary "cradle-like" features were also found where the reinforcements had been pulled away radially. Whiskers

oriented with their axes perpendicular to the direction of crack growth were typically broken flush with the fracture surface. Only a few were found protruding from the specimens, and in these cases the elevation was at most a few microns. Indentation cracks on the polished surfaces of the whisker specimens showed rare cases of short pullouts. Infrequent examples of bridging existed but it was not possible to conclusively determine whether bridging was caused by the matrix or whiskers. In general the fracture path suggests that the cracks propagated along the matrix/SiC(w) interface until they reached a weak point or a previously-fractured section of the whisker. The crack then broke through the whisker on a plane generally perpendicular to the length of the reinforcement, and continued to grow along its original direction. For both types of fractures, the exposed surfaces of the reinforcements were fairly clean of matrix material. Likewise, no SiC fragments were found in the empty "cradles." There was no evidence of processing-induced whisker surface damage.

It is clear that the defects observed in the Tateho whiskers used for these samples precluded achieving anticipated toughening, as has been observed with continuous SiC fibers and with SiC whiskers in RBSN matrices. Microstructural analyses of whisker-matrix interfaces, whisker dispersion in the matrix and strength controlling flaw dimensions all suggest that anticipated toughening would have been realized with better quality whiskers. Unfortunately, the highly perfect VLS whiskers synthesized by Los Alamos National Laboratory were no longer available for this research program. Analysis of a few experimental samples made with the Los Alamos SiC whiskers and the MIT Si powder exhibited very long pullouts and completely undamaged whisker surfaces after fracture.³³ These SiC whisker experiments demonstrate the postulated suitabilities of the processing technique and of the materials that were used.

- **Dimensional Stability:** Minimal dimensional change during the consolidation process is another important feature of this reaction formed material. From die to fired part, the total dimensional change for most RBSN parts is in the range of 0.25% without cold isostatic pressing (CIP'ing) and approximately 2.5% with a CIP'ing step; standard deviations are a few tenths of a percent in both cases.^{5,34} While impressive when compared to shrinkages observed with conventional densification processes (10-20%), filled RBSN samples allow even tighter tolerances to be maintained. For parts made from a mixture of 88% Si and 12% SiC SiH₄ derived powders, the total dimensional change was $0.1 \pm 0.05\%$. (A 1-inch die would produce a part that is 0.999 ± 0.0005 inches.) While the cost-savings of a net-shape fabrication process is the most evident consequence of achieving these dimensional tolerances, eliminating the uncontrolled flaw population that results from grinding will probably prove to have greater importance.
- **Toughness Measurements and Analyses:** Initially, fracture toughnesses of the RBSN and RBSN/SiC composites were measured by the indentation crack-length technique, and also by identifying the strength controlling flaw, then calculating the

toughness from the flaw dimensions and stress at the site.^{17,35} Both types of results are reported in Table 1. Although the indentation crack-length technique has been widely used for RBSN and other porous, brittle materials because it is rapid and inexpensive, our measurements by this technique did not reveal the same batch-to-batch variability revealed by the fractography technique.^{5,18} Extensive analyses convinced us that the apparent variations in toughness were real, and that the indentation crack-length technique lacked adequate sensitivity for purposes of improving the process. Because the fractography technique was so time consuming and it did not permit analysis in terms of possible R-Curve behavior, alternative measurement techniques were evaluated in terms of providing precise results rapidly with our standard sample configuration. The same sample geometry was retained to negate possible size effects which would prevent comparison of future results with a rather extensive existing data base.

An indentation-strength method was developed for measuring R-Curve behavior of ceramics in general, and the fracture toughness of these porous materials in particular.^{18,19,36} The technique for measurement of toughness by indentation-strength method, originally developed for materials that do not exhibit R-Curve behavior, was extended in a general way to the measurement of fracture resistance, K_R , for materials that exhibit a rising toughness with crack size. By using the assumption that the R-Curve can be described by a power-law function of crack size, it was shown that the equation for K_R in terms of the post-indentation strength was similar in form to the well known equation for K_C for constant toughness materials. Using the new equation, the R-Curve was evaluated by the indentation-strength technique for two materials that showed evidence of R-Curve behavior, namely, a fully dense alumina, AD 995, and a porous RBSN reinforced with approximately 38 vol% of 15 μm diameter SiC particles. Briefly, the technique involves conducting multiple post-indentation-strength measurements at several indentation loads. The R-Curve determined by this indentation-strength method agreed with the fracture resistance data obtained using the single-edge pre-cracked beam (SEPB) method for the alumina material. An additional advantage of this indentation-strength technique is that statistical analysis of the R-Curve can be done in a simple and straightforward manner using multiple specimens as in strength or toughness testing.

The evaluation of toughness of brittle materials by indentation methods is based on the premise that significant residual stresses are present beneath the indenter.³⁷ In porous materials there is the possibility that these residual stresses may not be sustained because of crushing effects, such as by pore collapse or densification beneath the indenter. The applicability of indentation methods to porous materials was carefully evaluated before they were extensively applied to the toughness and R-Curve determination of the RBSN composites of this program. The presence of residual stresses was critically assessed in both unreinforced RBSN and SiC particle reinforced RBSN composites.¹⁸ First, the apparent toughness in a post-indentation strength test

was determined, assuming that residual stresses are absent. This apparent toughness was then compared with the true toughness, or toughness associated with natural strength controlling flaws in the porous materials. The latter was evaluated by the fractography method involving measuring of strength controlling flaw sizes in the SEM and relating these to the stress at the flaw site. When large residual stresses are present, the ratio, A , of the apparent to true toughness is theoretically predicted to have the value of 0.47. We obtained an experimental average value of A of 0.43, indicating that large indentation residual stresses are present in our porous RBSN and RBSN composite samples.

As shown in Table 1, the K_{IC} values defined by indentation-strength and fractography techniques agree closely on an absolute basis, and show the same trends in batch-to-batch variations for RBSN and composite samples. In contrast, the widely used indentation crack length method did not reveal batch-to-batch variations in toughness.

- **Development of Fundamental Toughening Models:** To obtain quantitative estimates for the effects of candidate reinforcements, we developed a model for toughening by whisker or fiber reinforcements. This model predicted the composite-to-matrix toughness ratio based on assumed values of interface bonding, interface friction, fiber volume fraction, modulus, etc. Toughening was assumed to result from bridging of crack faces by unbroken fibers or whiskers in the wake of the crack. In the model, fibers or whiskers are allowed to debond over specified debond lengths on either side of the crack face, with a frictional resistance exerted on the crack faces in the debonded zone.

Solutions were first obtained for the mechanics of debonding of fibers and whiskers in the crack wake. These debonding solutions were then used to derive expressions for the steady-state toughnesses expected in these bonded composites. The final closed form expression for the steady-state composite toughness is given in Eq. (26) in citation number 8 of PUBLICATIONS RESULTING FROM DAAL03-88-K-0099. The predicted dependences of the toughness increase, ΔK , as functions of fiber volume fraction and fiber strength are shown for the SiC reinforced alumina system in Figures 6 and 7 respectively. The dependence of the composite toughness on the toughness of the fiber/matrix interface is shown in Figure 8. It is evident that the magnitude of the composite toughness is very sensitive to microstructural and interface and fiber strength values.

Composite-to-matrix toughness ratios in the range 5–10 appear attainable on the basis of this model for both SiC/Al₂O₃ and SiC/Si₃N₄ composite systems. This magnitude of toughening is generally larger than is expected for brittle-particle reinforced systems.

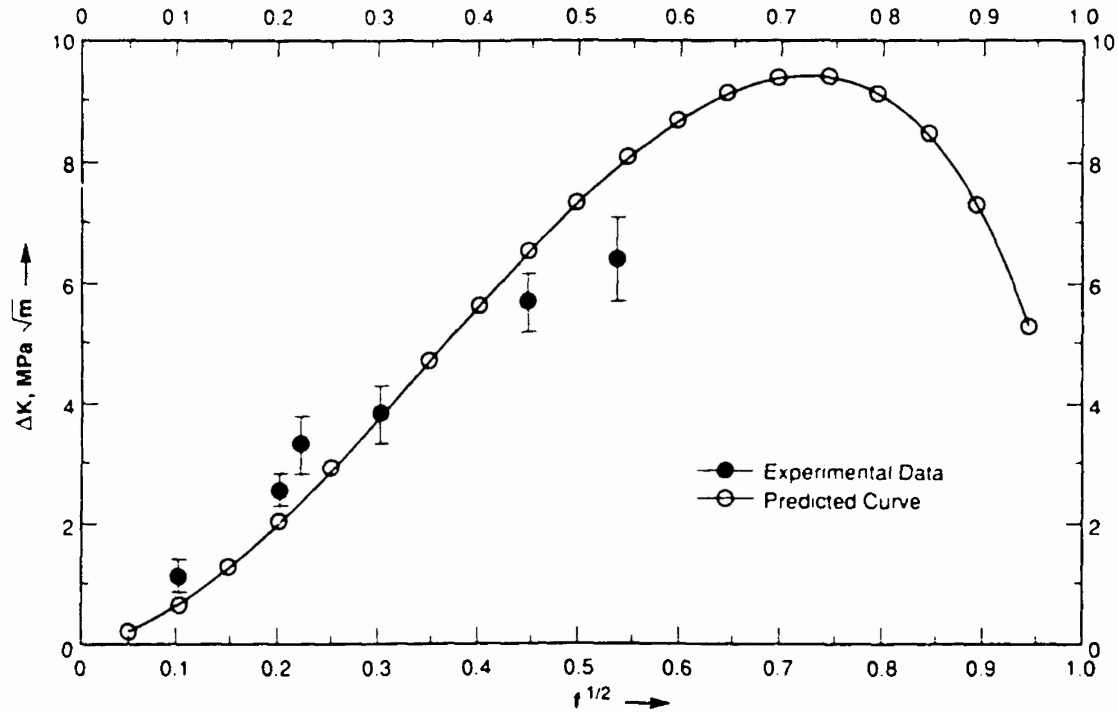


Figure 6. Increase in toughness due to fiber bridging as a function of the volume fraction of reinforcements. Solid line is the model prediction using Eq. (26) in citation number 8 of PUBLICATIONS RESULTING FROM DAAL03-88-K-0099 with $\sigma_f = 8$ GPa, $\tau = 100$ MPa, $G_{ic} = 6$ J/m². Data points pertain to SiC-whisker-reinforced alumina from P.F. Becher, C.-H. Hsueh, P. Angelini, and T.N. Tiegs, "Toughening Behavior in Whisker-Reinforced Ceramic Matrix Composites," *J. Am. Ceram. Soc.*, **71** [12] 1050-61 (1988).

Table 3. Material Property Values Used for Al₂O₃/SiC Composite System*

Property	Matrix (Al ₂ O ₃)	Fiber (SiC)
Modulus (GPa)	400	550
Toughness (MPa·m ^{1/2})	3.0	4.0
Radius (μm)		0.4
Poisson's ratio	0.23	0.19

* Numbers correspond to the material studied comprehensively in P.F. Becher, C.-H. Hsueh, P. Angelini, and T.N. Tiegs, "Toughening Behavior in Whisker-Reinforced Ceramic Matrix Composites," *J. Am. Ceram. Soc.*, **71** [12] 1050-61 (1988).

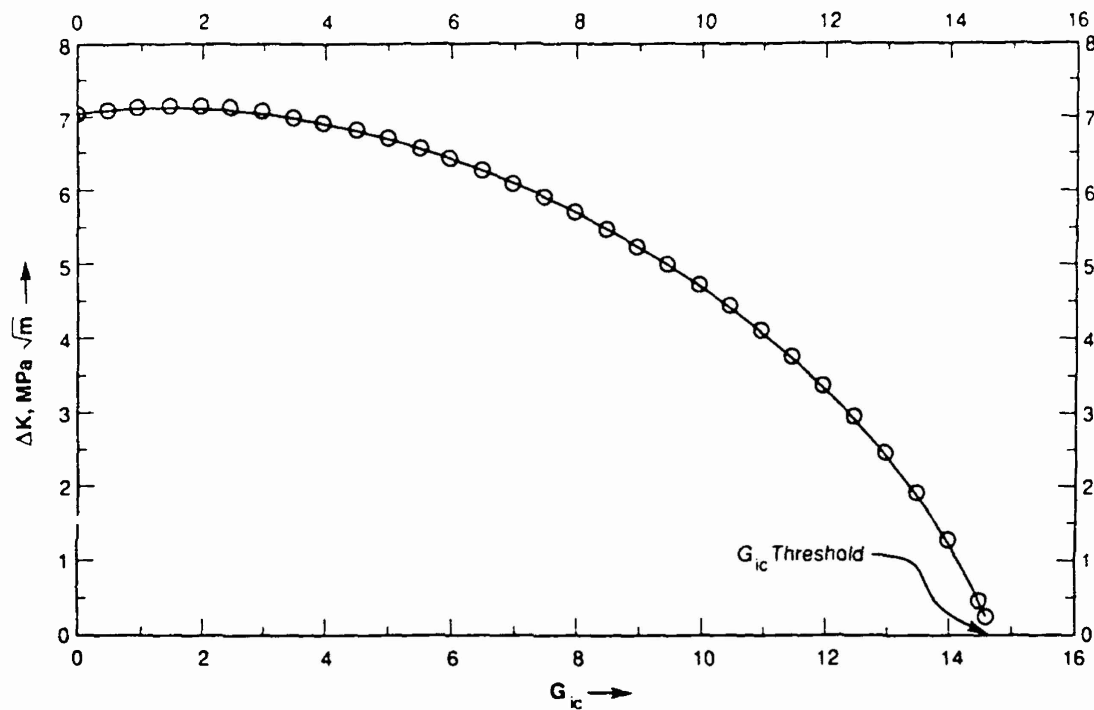


Figure 7. Prediction of toughness increase as a function of the interface toughness, G_{ic} , for material property values in Table 3. $\sigma_f = 8 \text{ GPa}$, $\tau = 100 \text{ MPa}$. The curve shows a peak at an intermediate value of G_{ic} . Experimental data at $G_{ic} = 6 \text{ J/m}^2$ is not the optimum value of G_{ic} .

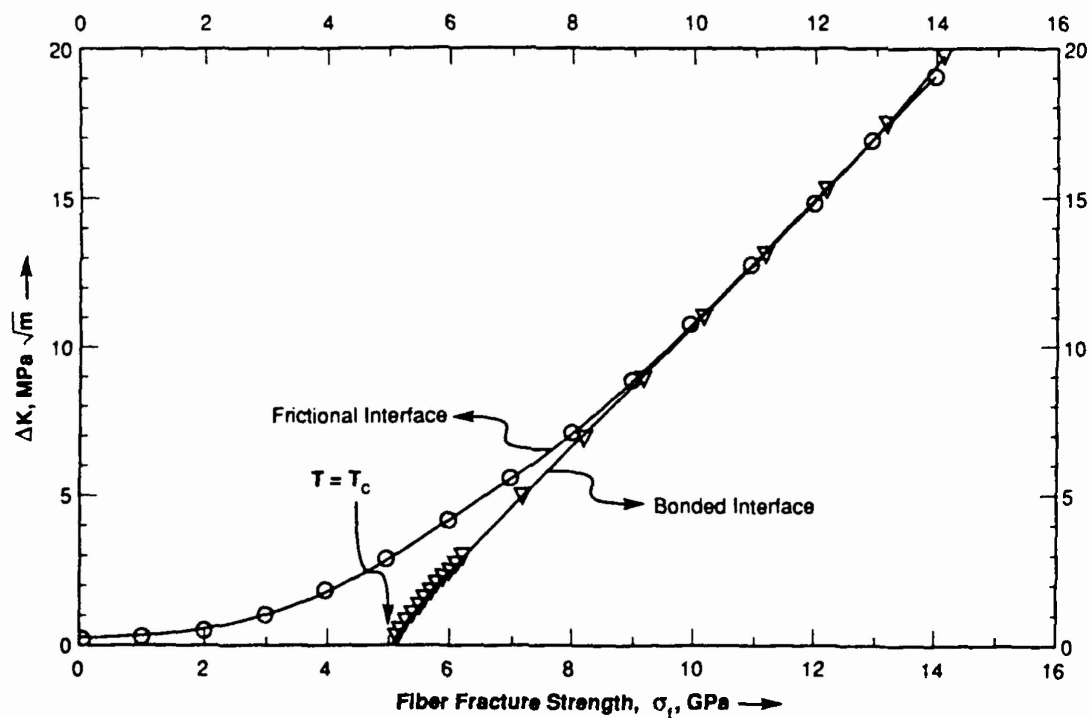


Figure 8. Prediction of toughness increase as a function of fiber or whisker fracture strength for material property values in Table 3. $\tau = 100 \text{ MPa}$, $G_{ic} = 6 \text{ J/m}^2$. Also shown for comparison is the corresponding toughness if the reinforcement and matrix were unbonded.

- **Nitriding Kinetics:** Even though nitriding kinetics was not originally intended to be a major thrust for this research program, related issues made nitriding critical for successfully synthesizing composites based on SiC reinforcements. Excessive nitriding times, nitriding temperatures or impurity levels (either intentional or accidental) cause the SiC to be at least partially converted to Si_3N_4 . Though more subtle, the same factors define the level of bonding between matrix and reinforcement phases, and thus play a pivotal role in achieving improved properties. For these reasons, nitriding kinetic issues related to the fabrication of SiC reinforced RBSN matrix composites were integrated with other nitriding research activities.

Through nitriding kinetic research, we have significantly reduced the severity of the nitriding schedules needed to convert the Si to high purity Si_3N_4 . If as-synthesized purity levels are maintained with the high purity Si powders, complete nitridation can be accomplished in schedules like 1150°C for 1h or 1250°C for 10m.^{27,28,38} The use of pre-nucleation heat treatments can reduce the required temperature to 1050°C .²⁷ Higher temperatures are required if the initial hydrogenated particle surface chemistry is altered by significant oxidation, alcohol or specific polymer exposures; however, the maximum required temperatures can remain as low as 1250°C and are always less than 1400°C .³⁹ These results represent dramatic reductions from conventional schedules with temperatures frequently in excess of the Si melting point and times up to 500 hours,^{33,40} which makes control of the microstructures and of interfaces in composites virtually impossible. Simply exceeding the Si melting temperature usually causes the liquid Si to flow uncontrollably in the RBSN part, where it typically collects in regions that are too large to nitride completely. Also, the volumetric expansion that occurs with solidification of Si can crack the parts. With the high purities of these materials and the moderate nitriding schedules, SiC particles, fibers (SCS-6) and whiskers have been incorporated into the RBSN matrix without adverse interactions.

Binders and solvents must be used to produce material with practical sizes, shapes, and densities. Similar to oxidation, these additives affect the surface chemistry and nitridation kinetics.^{28,39} Optimum binders and solvents will minimize adverse changes in the powders' surface chemistry. These changes can result directly through reactions with both the binder and solvent, as well as the ambient atmosphere used for binder burnout. Indirectly, the heating schedules used for binder burnout and other processing requirements attributable to the binder can make the powders vulnerable to oxygen and other agents. Both types of adverse effects must be minimized.

The effects of exposures to candidate solvents and binders on the nitriding kinetics of the SiH_4 derived Si powders have been investigated. Table 4 summarizes the polymer and solvent systems that were investigated. Polyethylene (PE) and polystyrene (PS) are both simple hydrocarbons which burn out cleanly and are used in injection molding.

Table 4. Polymer/Solvent Systems Investigated

<u>Binder</u>	<u>Formula</u>	<u>Solvent</u>	<u>Stab Wt T (°C)</u>	<u>Max T (°C)</u>
Polyethylene(PE)*	[CH ₂] _n	-	490	600
QPAC™ 40**	[C ₄ H ₆ O ₃] _n	Methanol	500	500
Polystyrene(PS)***	[C ₆ H ₅ CHCH ₂] _n	Xylene	460	600
Teflon(TFE)**** + Polystyrene***	[CF ₂] _n	Stoddard	580	600
Polysilazane (PSZ)*****	$\left[\begin{array}{l} [\text{CH}_3\text{SiHNH}]_{0.39} \\ [\text{CH}_3\text{SiHNCH}_3]_{0.04} \\ [\text{CH}_3\text{SiN}]_{0.57} \end{array} \right]_n$	Toluene	> 750	750

* A735 Polyethylene wax, Allied Signal Co., Morristown, NJ 07960

** QPAC™ 40, Lot 10021-30, Air Products and Chemicals, Inc., Emmaus, PA 18049

*** Polystyrene -- supplied by NASA-Lewis

**** Teflon®, E.I. DuPont de Nemours & Co., Inc., Wilmington, DE 19898

***** Polysilazane M. Wt. 6000-8000, proprietary composition, Ethyl Corp., Baton Rouge, LA 70801; indicated composition proposed by Wiseman for a similar polymer

Qpac™ is a binder that has been designed to burn out cleanly in a nitrogen atmosphere.⁴¹ The tetrafluoroethylene was added to the polystyrene (TFE/PS) to facilitate flow during pressing in the fabrication of SiC reinforced RBSN. The polysilazane (PSZ) was interesting for several reasons. PSZ forms a Si, N and C containing ceramic product upon pyrolysis⁴² that is space-filling and evolves smaller amounts of gaseous products which need to escape during the burnout. These features should enhance the microstructural quality. The PSZ residue may protect the silicon particle surfaces and also may offer an alternative reaction site for parallel nucleation of crystalline Si₃N₄. One concern is that PSZ films may block the silicon vapor transport and therefore limit the fast reaction rate.^{27,28}

Observed effects of exposures to the polymers on nitriding kinetics at 1250°C in N₂ are summarized in Figure 9. Several general observations can be made about the effects the investigated polymers had on the nitriding kinetics of the high purity Si powders.

PE/PS: These relatively simple hydrocarbons burn out cleaner, and only delay the onset of the nitriding reaction. For PE, it appears that this results from some reduction in the nucleation rate (based on the longer induction time, the slightly lower conversion, and the estimated number of nuclei per

particle). PS, however, demonstrated similar nitriding results apparently with a relatively high number of nuclei. These results suggest that surface contamination with simple hydrocarbons does not inhibit nitridation as severely as surface contamination from oxygen, alcohol, and the other polymers that were studied. After extended induction periods, fast reaction rates and ultimate conversions to Si_3N_4 were essentially the same as observed with pure Si powders.

TFE/Qpac: These binders contain oxygen and fluorine in addition to carbon and hydrogen. These apparently cause more serious surface contamination which leads to incomplete conversion at low temperatures. The data suggest excessive nuclei are responsible for the inhibited reactions despite an initial nucleation barrier. A significant amount of Si is lost by vaporization from the TFE samples.

PSZ: By design, the Si-N-C-H polymer leaves 75% residue behind after binder burnout, which significantly alters the particles' surfaces. The relatively high number of estimated nuclei per particle suggests that Si_3N_4 might actually nucleate within this residue.

At the end of binder burnout there is little Si-N bonding and the protective Si-H surface is lost, leaving powders vulnerable to oxidation.^{27,28,39} Slow heating rates and lengthened induction periods resulted in significant oxidation. Use of gettered nitrogen, correct polymers and faster heating rates, when the binder will allow, will minimize this oxidation. Other residues from the polymers can accentuate or negate the effect of oxygen on nitriding kinetics. Oxidation does not effectively retard nitriding kinetics when there is hydrocarbon bonding on the silicon surface. The same effect has been observed previously when free carbon is present in the form of high purity carbon-rich SiC.⁴³ In contrast, residues from more complex polymers significantly retard nitriding kinetics, apparently by accentuating oxygen's effects.

Several additional phenomenological generalizations can be made.³⁹ If samples with uncertain initial binder content are excluded, the weight gained during the induction period is proportional to the length of the induction period. The reaction kinetics suggest several optimizations which may be necessary to achieve rapid conversion at minimum temperatures. The number of nuclei which form per silicon particle should be < 100 . An induction period weight gain of about one weight % maximizes the fast reaction rate. A peak reaction rate of at least 15% per minute seems necessary to achieve full conversion of the $\sim 0.25 \mu\text{m}$ diameter Si particles during the fast period at 1250°C . Polymer exposed samples showing incomplete conversion at 1250°C nitride to completion after the 1400°C 10h schedules. It has been shown that these extended schedules do not damage the SiC reinforcements.^{19,32} In general, these results indicate

that reasonable nitridation rates at relatively low temperatures are possible with the use of the proper polymers.

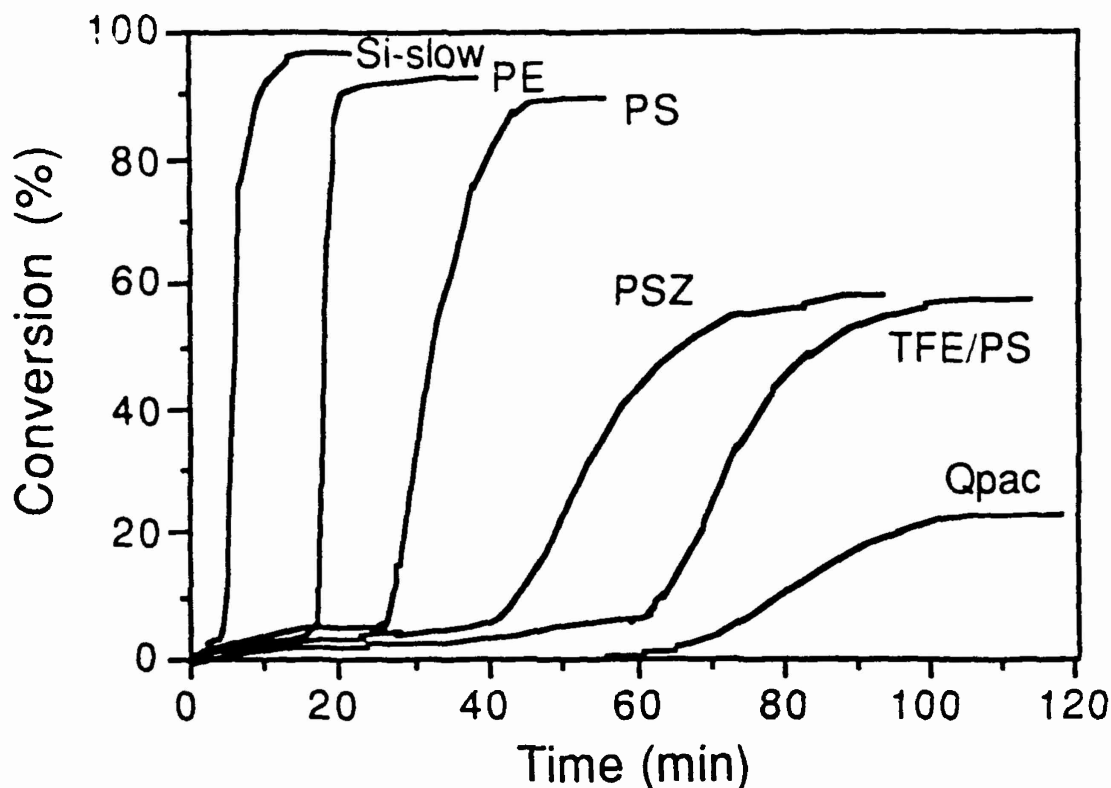


Figure 9. A summary of the 1250°C TGA nitriding kinetic results for Si samples made from polymer exposed high purity Si powders and a Si reference (reference 39). Polyethylene (PE) and polystyrene (PS) are both simple hydrocarbons which burn out cleanly and are used in injection molding. QPAC™ is a binder that has been designed to burn out cleanly in a nitrogen atmosphere. The tetrafluoroethylene was added to the polystyrene (TFE/PS) to improve particle flow during pressing. The polysilazane (PSZ) was investigated as a nonfugitive, preceramic polymer. The heating schedule used for the Si-slow reference duplicated the time-temperature histories used for the polymer exposed samples.

III. CONCLUSIONS AND SUGGESTIONS FOR CONTINUED RESEARCH

This research program has shown that characteristic deficiencies generally associated with porosity in brittle materials are not intrinsic, and that many potentially advantageous properties can be realized through appropriate processing strategies. Based on these results, it can be concluded that reaction formed ceramics will be able to compete favorably with conventional, fully dense ceramics in many applications demanding maximum properties. Simultaneously, the use of SiH_4 derived Si powder has permitted many long standing problems with reaction bonded silicon nitride (RBSN) to be resolved.

Using the small diameter, high purity powders permitted complete nitridation to be completed in combinations like one hour at 1150°C or ten minutes at 1250°C without using property degrading nitriding accelerators like CoO , NiO , FeO , etc. With prenucleation, parts made from the high purity Si powders can be completely nitrided in one hour at 1050°C . These nitriding schedules are much less severe than conventional schedules which generally include temperatures which exceed the melting point of Si and last for periods up to several hundreds of hours. These reduced schedules and high purities permit reinforcements, such as SiC , to be incorporated without chemical attack and retention of properties to previously inaccessible temperature levels.

RBSN samples containing 25% porosity were made that exhibited strengths up to 870 MPa, levels previously only achieved with fully dense Si_3N_4 samples having much higher fracture toughnesses. It was concluded that high strengths can be achieved by distributing residual porosity uniformly in ultrafine pores and avoiding formation of larger microstructural defects. It is also concluded that, rather than being damaging, the porosity in the RBSN improves specific strength (up to $0.36 \text{ MPa}/(\text{kg}/\text{m}^3)$) by reducing the density, and improves strain to failure ($\sim 0.3\%$) by reducing the elastic modulus.

High purities in combination with short, low temperature nitriding schedules permitted particulate (p) and whisker (w) based composites to be made successfully with SiC(p) and SiC(w) reinforcements. The particulate composites exhibited anticipated toughening. For the case of reinforcement by $15 \mu\text{m}$ size SiC particles the fracture toughness increased by a factor of about 1.4 to 1.6, and by a factor of about 1.9 for the $50 \mu\text{m}$ size SiC particle reinforcement. Also, reinforcement by $15 \mu\text{m}$ size SiC particles showed evidence of R-Curve behavior when the SiC volume fraction was sufficiently high (about 38 vol%). The composites made with SiC(w) reinforcements did not exhibit anticipated improvements in toughness even though matrix to whisker bonding fulfilled desired criteria because the whiskers contained excessive microstructural and morphological defects. The composite experiments demonstrated the feasibility of improving the toughness of RBSN.

The fine pore structure, responsible for the high strengths, and the high purity, responsible for the enhanced nitriding kinetics, combined to give superior oxidation resistance. At 1000 and 1400°C oxidation rates were 10-20 times less than is observed either with high quality RBSN or fully dense hot pressed Si_3N_4 at the same temperature levels. Rapid

formation of exceptionally thin protective layers on the high purity RBSN eliminated the usually observed loss in strength that results largely from cracks which form in the thick SiO_2 films during cooling, and which then propagate into the Si_3N_4 substrate.

Extremely small dimensional changes were also demonstrated. With unfilled Si, the shrinkage from the die dimensions to the nitrided part was generally less than 0.25% without cold isostatic pressing (CIP'ing) and approximately 2.5% with a CIP'ing step; standard deviations were a few tenths of a percent in both cases. Filled RBSN samples allow even tighter tolerances to be maintained. For parts made from a mixture of 88% Si and 12% SiC powders, the total dimensional change was $0.1 \pm 0.05\%$. (A 1-inch die would produce a part that is 0.999 ± 0.0005 inches.) Net shape forming was demonstrated with exceptional dimensional control. The absence of shrinkage is particularly important for making composites that are free of liquid phase sintering aids.

This research has shown the potential that porous, reaction formed ceramics, like RBSN, have for even the most demanding applications. It has also shown that important issues remain.

Although trends have been identified, the underlying basis for the variation in fracture toughnesses exhibited by the unreinforced, porous matrices remains largely undefined. Extensive and careful characterizations of batches of RBSN exhibiting high and low toughness values revealed differences that are consistent with the toughness levels. The lower toughness material contained larger pores, smaller grain sizes and lower levels of lattice strain than the tougher material. There is some evidence that these differences are traceable to the characteristics of the starting Si powders that were employed. Until models for the mechanical properties of intermediate density brittle materials are developed, optimization of microstructural features must be conducted through empirical manipulation of process variables.

Fabrication of parts with practical shapes and dimensions will require the use of binders and solvents. Research to date has shown that the nitridation kinetics are extremely sensitive to the surface chemistry of the high purity Si powders. This research has also shown that while simple hydrocarbons like polyethylene and polystyrene delay the onset of the nitriding reaction they do not inhibit it once it begins. The interaction between surface chemistry, nitriding atmosphere, exposure history and nucleation and growth kinetics will require extensive study before they are understood. Fortunately, these studies can be initiated with solvent and polymer systems which have a high probability of meeting all requirements.

IV. PUBLICATIONS RESULTING FROM DAAL03-88-K-0099

PAPERS

1. **Strength of Reaction Bonded Silicon Nitride After High Temperature Air Exposures**, J.E. Ritter, P.A. Gennari, S.V. Nair, J.S. Haggerty, and A. Lightfoot, 13th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1989, published in CERAM. ENG. SCI. PROC. **10** [7-8] 625-31 (1989).

ABSTRACT

The effects of high-temperature exposures on the room-temperature strength of RBSN made from high purity Si powder have been studied. Oxidation at 1000°C in air for 1h revealed no evidence of an oxide layer by SEM, and only a ~0.6 µm layer after 50h. After oxidation at 1400°C, SEM indicated a ~0.5 µm layer formed in 1h and a ~1.5 µm layer formed in 50h. The 1400°C-50h layers exhibited a uniform 3-5 µm crack pattern; however, these cracks did not penetrate into the RBSN substrates. Contrary to conventional RBSN, these oxidizing exposures did not change the strength or the fracture toughness of the high purity RBSN ($MOR = 435 \pm 120$ MPa and $K_{IC} = 2.1 \pm 0.5$ MPa·m^{1/2}). This superior oxidation resistance resulted from the purity and the small channel diameters achieved in the SiH₄ derived RBSN.

2. **Nitriding Kinetics of Si-SiC Powder Mixtures as Simulations of Reaction Bonded Si₃N₄-SiC Composites**, A. Lightfoot, B.W. Sheldon, J.H. Flint, and J.S. Haggerty, 13th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1989, published in CERAM. ENG. SCI. PROC. **10** [9-10] 1035-48 (1989).

ABSTRACT

The nitriding kinetics of Si and Si plus SiC powder mixtures were studied to simulate the fabrication of RBSN-SiC ceramic matrix composites. Very clean, as-synthesized and solvent-exposed powders were studied; C-rich and Si-rich SiC 0.04-0.05 µm diameter powders were mixed in varying concentrations with SiH₄-derived 0.2-0.3 µm diameter Si powder. Reactions were monitored with TGA and samples were characterized by SEM and X-ray diffraction. Although all exposures inhibited the nitriding kinetics from rates observed with the as-synthesized Si powders, complete conversion was still achieved with nitriding schedules that permit fabrication of composites. For example, complete nitridation is achieved with C-rich SiC powders in 140 minutes at 1250°C, and in the centers of Si-rich SiC powders in 15 minutes. The effects on the incubation periods, fast reaction periods and slow reaction periods that characterize these nitriding processes were studied to explain unusual reverse reaction gradients and other effects of contaminations.

3. **The Formation of Reaction Bonded Si₃N₄ at Low Temperatures and in Short Times**, B.W. Sheldon, and J.S. Haggerty, 13th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1989, published in CERAM. ENG. SCI. PROC. **10** [7-8] 784-793 (1989).

ABSTRACT

The kinetics and mechanisms of nitriding high purity, SiH₄ derived Si powders were investigated. TGA, X-ray diffraction, FTIR spectroscopy, and TEM techniques were employed. Complete nitridation (>99%) was achieved at 1250°C in less than 10 minutes, and nearly complete nitridation (97%) was achieved at 1100°C in less than 5 hours. The effects of temperature, particle diameter, and surface chemistry were

studied and results show that the process is principally controlled by the number of Si_3N_4 nuclei that form. Reduced temperature, increased Si particle diameter, and surface contamination all reduce the conversion rate through direct effects on nucleation.

4. **Oxidation and Fracture Strength of High Purity Reaction Bonded Si_3N_4** , J.S. Haggerty, A. Lightfoot, J.E. Ritter, P.A. Gennari, and S.V. Nair, J. AM. CERAM. SOC. **72** [9] 1675-79 (1989).

ABSTRACT

Reaction bonded Si_3N_4 (RBSN) made from high purity Si powder is unusually resistant to degradation caused by exposures to air for up to 50h at temperatures up to 1400°C . The weight-gain during oxidation of this SiH_4 originating RBSN is approximately ten times less than conventional RBSN. Contrary to normally observed strength degradations, room-temperature strengths of this high purity, oxidized RBSN (ave. = 435 MPa, max. = 668 MPa) remained at their unusually high, as-processed levels after 1000 and 1400°C oxidizing exposures. Fracture toughness values were unaffected by oxidation ($K_{IC} = 2.3\text{-}2.4 \text{ MPa}\cdot\text{m}^{1/2}$). This superior oxidation resistance results from the high purity and the small diameter pore channels ($0.01\text{-}0.06 \mu\text{m}$) achieved in this SiH_4 originating RBSN.

5. **Reaction-Based Processing Methods for Ceramic-Matrix Composites**, Y.-M. Chiang, J.S. Haggerty, R.P. Messner, and C. Demetry, AM. CERAM SOC. BULL. **68** [2] 420-428 (1989).

ABSTRACT

Recent understandings of the severe limitations to densification of crystalline, ceramic matrix composite systems have underscored the need for processes that are capable of forming composite matrices *in situ* without shrinkage. This paper reviews reaction-forming methods for processing ceramic matrix composites that are appropriate for fiber, whisker and particulate reinforcements. Although some of these processes have not been widely applied to fiber-reinforced composites, all appear to have that potential. In addition, most are suitable for the processing of near-net shape, near-net dimension monolithic ceramics. We review and discuss the relative merits of approaches based on condensed-phase : gas-phase reactions, and condensed-phase : condensed-phase reactions.

6. **Reaction Based Processing Methods for Ceramics and Composites**, J.S. Haggerty, and Y.-M. Chiang, 14th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1990, published in CERAM. ENG. SCI. PROC. **11** [7-8] 757-781 (1990).

ABSTRACT

Reaction forming methods successfully applied to ceramic monoliths and composites having a wide range of compositions are reviewed. Net-shape capabilities and the potential for high purity are the principal advantages of this processing route for both monoliths and composites. Recent results with several different processing techniques demonstrate that superior, often unique, properties can be achieved with these materials if correct microstructural features are achieved. The absence of shrinkage is particularly important for composites because sintering aids are not needed to facilitate particle and reinforcement rearrangements during densification. The absence of sintering aids can allow monoliths and composites both to retain improved properties to higher temperatures. Approaches based on condensed-phase :

gas-phase reactions and condensed-phase : condensed-phase reactions will be discussed.

7. **Properties of RBSN and RBSN-SiC Composites**, A. Lightfoot, H.L. Ker, J.S. Haggerty, and J.E. Ritter, 14th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1990, CERAM. ENG. SCI. PROC. **11** [7-8] 842-856 (1990).

ABSTRACT

Strengths, fracture toughnesses, hardnesses, and dimensional changes have been measured for RBSN and RBSN/SiC composites. Samples were made from mixtures of Si and either Si- or C-rich SiC powders. All powders were derived from SiH₄. Dimensions of the nitrided composites were essentially equal to those of the dies (for RBSN + Si-rich SiC, total change = $0.1 \pm 0.05\%$). For pure, 75% dense RBSN dispersed with octanol, strengths up to 858 MPa have been achieved. Improved strengths result from a combination of microstructural perfection and increased fracture toughness. Toughnesses were measured by the indentation technique and through fracture mechanics analysis of fracture origins. The mechanical properties of the composites were approximately equal to those of methanol processed RBSN but not quite equal to those of the octanol processed RBSN. Results are discussed in terms of observed microstructural features.

8. **Crack-Wake Debonding and Toughness in Fiber- or Whisker-Reinforced Brittle-Matrix Composites**, S.V. Nair, J. AM. CERAM SOC. **73** [10] 2839-47 (1990).

ABSTRACT

Solutions are obtained for the mechanics of debonding in the crack wake in fiber- or whisker-reinforced composites for the case where a finite shear traction exists at the fiber/matrix interface in the debonded zone. These solutions are then applied to derive expressions for the steady-state toughness increases obtained in bonded composites wherein the toughness contribution is provided by crack-wake fiber/matrix debonding and crack bridging. The solutions for an unbonded composite containing a frictional fiber/matrix interface can be obtained from the derived equations in the limit of the fiber/matrix interface toughness equal to zero. In this limit, the debond crack length reduces to the slip length and the expressions for the crack opening and the predicted toughness increase reduce to previously derived expressions for unbonded composites. The steady-state toughness is found to depend sensitively on the interface toughness, the fiber fracture strength, and the shear tractions in the debonded zone including other material parameters, such as fiber radius and volume fraction and the moduli of the constituent phases. It is shown that in order to obtain finite toughness increases, the fiber/matrix interface toughness must be less than a critical value dependent on the fiber fracture strength, fiber radius and volume fraction, and fiber and matrix moduli. The predictions of the model are applied to published experimental results from a detailed and complete study of toughness increases in a bonded whisker-reinforced composite.

9. **High Performance, Porous, Brittle Structural Ceramics**, J.S. Haggerty, 37th Sagamore Conference, on Structural Ceramics, Plymouth, MA, October 1990, published in Sagamore Army Materials Research Conference Proceedings, pp. 307-316.

ABSTRACT

Traditionally with brittle materials, acceptable properties have only been achieved with low porosities. With very few exceptions, the thrust of ceramics processing research has been one of minimizing both porosity and grain size while achieving a desired phase chemistry. Sintering aids, that degrade high temperature performance, are usually an essential feature of this strategy.

Our results with reaction bonded silicon nitride (RBSN) show that porous brittle materials can exhibit properties that equal or exceed those of their fully dense counterparts provided that they are made with the same level of perfection as is sought in the traditional materials. With over 25% interconnected porosity, we have achieved strengths up to 870 MPa, oxidation resistances up to 20 times lower than fully dense Si_3N_4 , and no loss of strength after oxidizing exposures. Strength-to-weight and strain-to-failure values for these materials exceed those of fully dense Si_3N_4 . These results are understood in terms of fracture mechanics and the uniquely high purities that can be achieved with reaction formed ceramics.

The RBSN results serve as a model for other materials and reveal opportunities for making ceramic parts based on processes that have been avoided because they tend to leave levels of porosity that have been considered unacceptable. These net-shape processes appear capable of producing unique parts with equal or improved properties. Examples from our own work as well as of polymer derived and composite parts will be discussed.

10. **High Strength, Porous, Brittle Materials**, J.S. Haggerty, A. Lightfoot, J.E. Ritter and S.V. Nair, Materials Research Society 1990 Fall Meeting, Boston, MA, November 1990, published in MAT. RES. SOC. SYMP. PROC. Vol. 207, pp. 71-76 (1991).

ABSTRACT

Contrary to existing models, strengths need not be a strong function of porosity for intermediate density, brittle materials. Flaw sizes can remain small ($<50\text{ }\mu\text{m}$) if the void space is distributed uniformly in minimum dimension pores. For RBSN, fracture toughness decreases linearly with porosity for $0 < \text{porosity} < 40\%$. Strains to failure and specific strengths of these materials are higher than fully dense counterparts.

11. **Processing and Properties of SiC Whisker and Particulate Reinforced Reaction Bonded Si_3N_4** , A. Lightfoot, L. Ewart, J. Haggerty, Z-Q. Cai, J. Ritter and S. Nair, 15th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, January 1991, published in CERAM. ENG. SCI. PROC. 12 [7-8] 1265-1291 (1991).

ABSTRACT

Intermediate density, high purity RBSN made from silane-derived Si powders has a specific strength and strain-to-failure higher than fully dense Si_3N_4 . Because the fracture toughness is comparatively low, this research sought to increase fracture resistance through composite toughening with particulate and whisker additions. The RBSN composites were made from colloiddally pressed octanol dispersions of 0.2-0.3 μm diameter, high purity Si powders mixed with either SiC whiskers, SiC(w), or Acheson α -SiC particles, SiC(p), having diameters of $\sim 0.5\text{ }\mu\text{m}$ and $\sim 2.0\text{ }\mu\text{m}$, respectively. The effect of the reinforcements on room temperature strength, fracture toughness and R-curve behavior, and interactions between cracks and reinforcements were studied. None of the materials exhibited R-curve behavior. While the

microstructural properties of the matrix were retained and no evidence of SiC surface degradation was observed, an increase in K_{IC} was seen only in the 33 vol% SiC(p). Details of the fracture process were revealed by SEM of surface cracks and fracture surfaces as well as TEM. Inoperative toughening mechanisms in the whisker composite were attributed to non-uniform whisker morphology. The modest increase in K_{IC} of the 33 vol% particulate samples resulted from crack deflection around larger particles.

12. **Mechanical Behavior of a Continuous-SiC-Fiber-Reinforced RBSN-Matrix Composite**, S.V. Nair, T.-J. Gwo, N. Narbut, J.G. Kohl, and G.J. Sundberg, J. AM. CERAM. SOC. 74 [10] 2551-58 (1991).

ABSTRACT

The results of a detailed study are presented on the toughening of reaction-bonded silicon nitride reinforced with large-diameter SiC monofilaments at ambient and elevated temperatures. Composite stiffness, strength, toughness, and *R*-curve behavior were investigated at ambient temperature, with strengths measured up to 1400°C. At elevated temperature, toughening mechanisms were explored by investigating crack initiation and growth under creep conditions. The results show that, at ambient temperature, the composite exhibited noncatastrophic failure with substantial toughening associated with contributions of both fiber pullout and elastic bridging of fibers in the crack wake, consistent with predictions using available models. Limited *R*-curve measurements suggest that large-scale bridging effects may be present. At elevated temperature, crack initiation occurred in the matrix at about 1000°C, but in the fiber at higher temperatures. Growth of cracks is governed by time-dependent bridging of unbroken fibers in the crack wake, consistent with a model based on fiber pullout by viscous sliding of fibers out of the matrix along amorphous interfacial layers.

13. **Nitridation of Binder and Solvent Exposed High Purity Silicon Powder**, A. Lightfoot, R.S. Parikh, J.S. Haggerty, and B.W. Sheldon, submitted to J. AM. CERAM. SOC.

ABSTRACT

High purity, submicron Si powders having hydrogenated surfaces made from SiH₄ gas nitride rapidly at unusually low temperatures. Exposures to polymers required for fabrication of parts alter the powders' surface chemistry directly through reactions with the polymers, or indirectly by making them vulnerable to effects made possible by elevated temperatures required for binder removal. The nitriding kinetics of SiH₄ derived Si powders exposed to polyethylene, polystyrene, Qpac™, tetrafluoroethylene/polystyrene and polysilazane binders have been studied. The surface chemistries of the powders after binder burnout in N₂ or vacuum were related to nitriding kinetics, and nitrided samples were characterized. Relatively long exposures to temperatures required for binder burnout are the primary cause for retardation or inhibition of the nitriding reactions through the effects of oxygen contamination; however, polymer residues can either accentuate or negate this effect. Simple hydrocarbon polymers, polyethylene and polystyrene, left a carbon residue (Si-C and Si-CH₃ bonding) which offset the inhibiting effect of oxygen to permit > 90% conversion after slightly extended induction periods. The others left more complex residues which extended the induction period, suppressed the fast reaction rate period, and caused premature termination of the fast reaction period. Exposure to tetrafluoroethylene had the most inhibiting effect and apparently caused Si losses. Each polymer had a different effect on the nucleation of Si₃N₄. SiC fibers were shown to have a negligible effect on the Si nitriding kinetics.

14. **Analyses of RBSN Having High and Low Fracture Toughnesses**, A. Lightfoot, J. Sigalovsky, and J.S. Haggerty, submitted to J. AM. CERAM. SOC.

ABSTRACT

By reducing flaw sizes, ~75% dense RBSN has been made which exhibits strengths up to 870 MPa, levels normally achieved only by fully dense Si_3N_4 . These strengths, combined with essentially zero shrinkage and excellent high temperature properties, make it an important candidate for matrices of ceramic composites. Detailed fractographic and micro-structural characterizations were undertaken because fracture toughnesses of nominally identical RBSN batches differed significantly (~ 2.0 to $\sim 2.7 \text{ MPa}\cdot\text{m}^{1/2}$) and existing behavioral models are inadequate for microstructural design or interpreting properties of brittle materials having this level of porosity. High and low toughness materials as well as constituent powders have been characterized by SEM/FEG, TEM, BET, XRD, and Hg-porosimetry; subtle differences have been revealed.

15. **Indentation Residual Stresses in RBSN and RBSN Composites**, S.V. Nair, P.Z.Q. Cai, J.E. Ritter, A. Lightfoot, and J.S. Haggerty, CERAM. ENG. SCI. PROC. 13 [7-8] 90-98 (1992).

ABSTRACT

The evaluation of toughness of brittle materials by indentation methods is based on the premise that significant residual stresses are present beneath the indenter. In porous materials, there is the possibility that residual stresses may not develop because of pore collapse, or densification, beneath the indenter. The presence of residual stresses was critically assessed using post-indentation strength measurements in a nanoporous reaction bonded silicon nitride (RBSN) and RBSN reinforced with SiC particulates which contain porosity levels on the order of 25%. The results showed the presence of significant residual stresses in these materials and the applicability of the indentation-strength method to toughness determination of the nanoporous materials was demonstrated. However, the indentation crack length method of toughness determination was unable to reveal variations in toughness between the different samples.

16. **Relationships between Toughness and Microstructure of Reaction Bonded Si_3N_4** , A. Lightfoot, J. Sigalovsky and J.S. Haggerty, CERAM. ENG. SCI. PROC. 13 [7-8] 1024-1031 (1992).

ABSTRACT

Fracture toughnesses of nominally identical batches of reaction bonded silicon nitride differed significantly (~ 2.0 and $\sim 2.7 \text{ MPa}\cdot\text{m}^{1/2}$). Detailed fractographic and microstructural characterizations investigated underlying factors. Subtle differences between high and low toughness RBSN and between constituent Si powders have been revealed through SEM/FEG, TEM, BET, Hg-porosimetry, and XRD. The results illustrate the need for behavioral models to guide microstructural design and to interpret properties of brittle materials with intermediate levels of porosity.

17. **Mechanical Behavior of Silicon Carbide Particulate Reinforced Reaction Bonded Silicon Nitride Matrix Composites**, S.V. Nair, P.Z.Q. Cai, J.E. Ritter, A. Lightfoot, and J.S. Haggerty, CERAM. ENG. SCI. PROC. 13 [7-8] 81-89 (1992).

ABSTRACT

SiC particulate reinforced reaction bonded Si_3N_4 composites were made by colloiddally pressing samples from octanol dispersions of commercial SiC particles with 0.2-0.3 μm diameter, high purity Si powders made from SiH_4 gas. SiC volume fractions in the range of 20-38 vol% were selected with two particle sizes of 15 and 50 μm . As-processed strengths of the particulate reinforced composites were determined in a ball-on-ring test. Fracture toughness and R-curve behavior of each composite type were measured by loading indented 3-point-bend bars to failure. Significant toughening was observed for both SiC particle sizes; however, strength degradation occurred in the 50 μm SiC(p) composite. This toughening appears to be due to crack bridging and microcracking of the SiC particles in advance of the propagating crack.

18. **Application of Indentation-Strength Method to R-Curve Measurements**, S.V. Nair, P.Z.Q. Cai, and J.E. Ritter, CERAM. ENG. SCI. PROC. 13 [7-8] 957-965 (1992).

ABSTRACT

Technique for the measurement of toughness by indentation-strength method, originally developed for materials that do not exhibit R-curve behavior, is extended in a general way to the measurement of the fracture resistance, K_R , for materials that exhibit a rising toughness with crack size. The R-curve was evaluated by this technique for alumina AD995 and a nanoporous RBSN reinforced with 38vol% of 15 μm SiC particles. The R-curve determined by the indentation-strength method agreed with fracture resistance data obtained independently for the fully dense alumina ceramic.

PRESENTATIONS (WITHOUT MANUSCRIPTS)

1. **Processing of Reaction Bonded Si_3N_4 - SiC Composites**, A. Lightfoot, F.M. Yee, H.-L. Ker, B.W. Sheldon, and J.S. Haggerty, presented at the 91st Annual Meeting and Exposition of the American Ceramic Society, April 1989, Indianapolis, IN.

ABSTRACT

Reaction bonded Si_3N_4 (RBSN) composites reinforced with SiC particles, platelets and whiskers have been fabricated. The RBSN matrix is based on high purity Si powder made from laser heated SiH_4 gas to take advantage of high strengths, excellent oxidation resistance and rapid nitriding kinetics exhibited by monolithic RBSN parts made from this material. High purity particulate reinforcements were either Si- or C-rich powders derived from SiH_4/CH_4 mixtures; platelets and whiskers were obtained from commercial sources.

Nitriding kinetics for composite parts made with varying amounts of the four types of reinforcements have been measured. Preliminary mechanical property (strength, fracture-toughness and hardness) measurements have been made. Results are compared to nitriding kinetic models and characteristics of pure RBSN.

2. **High Performance Reaction Bonded Silicon Nitride: A Model for Other SHS Formed Ceramic Materials**, J.S. Haggerty, presented at U.S. Army Materials Technology Laboratory meeting of SHS Working Group and BTI/DARPA Advanced Armor SHS Programs, August 1989, Watertown, Massachusetts.

ABSTRACT

Traditionally with brittle materials, acceptable properties have only been achieved with low porosities. With very few exceptions, the thrust of ceramics processing research has been one of minimizing both porosity and grain size while achieving a desired phase chemistry. Sintering aids, that degrade high temperature performance, are usually an essential feature of this strategy.

Our results with reaction bonded silicon nitride (RBSN) show that porous brittle materials can exhibit properties that equal or exceed those of their fully dense counterparts provided that they are made with the same level of perfection as is sought in the traditional materials. With over 25% interconnected porosity, we have achieved strengths up to 870 MPa, oxidation resistances up to 20 times lower than fully dense Si_3N_4 , and no loss of strength after oxidizing exposures. Strength-to-weight and strain-to-failure values for these materials exceed those of fully dense Si_3N_4 . These results are understood in terms of fracture mechanics and the uniquely high purities that can be achieved with reaction formed ceramics.

The RBSN results serve as a model for other materials and reveal opportunities for making ceramic parts based on processes that have been avoided because they tend to leave levels of porosity that have been considered unacceptable. These net-shape processes appear capable of producing unique parts with equal or improved properties. Examples from our own work as well as of polymer derived and composite parts will be discussed.

3. **Mechanical Behavior of a Continuous SiC Fiber Reinforced RBSN**, S.V. Nair, J.G. Kohl, J.E. Ritter, N. Narbut and G. Sundberg, presented at the 92nd Annual Meeting and Exposition of the American Ceramic Society, Dallas, TX, April 1990.

ABSTRACT

Reaction Bonded Silicon Nitride (RBSN) has been commercially established as a strong lightweight ceramic with excellent specific properties. In addition, it has the advantage of low processing temperatures which allows for the inclusion of fibers with a minimum of fiber degradation. Mechanical properties are presented in a non-commercial model composite RBSN containing double coated AVCO SiC fibers. Data is presented on room temperature tensile and bend properties and tensile R-Curve behavior. Data is also presented on elevated temperature creep fracture development using interrupted bend bar tests in air. Results indicate enhanced R-Curve behavior and contained fracture both at room and elevated temperature by fiber bridging.

4. **Nitriding Kinetics of Binder and Solvent Exposed High Purity Silicon Powder**, A. Lightfoot, R. Parikh, J.S. Haggerty, and B.W. Sheldon, presented at the 92nd Annual Meeting and Exposition of the American Ceramic Society, Dallas, TX, April 1990.

ABSTRACT

Fabrication of composites will require the use of polymers and solvents to achieve defect-free parts with required reinforcement architectures. Selection of optimum polymeric materials requires an understanding of the effects that surface chemistry and removal processing steps have on the nitriding behavior. This work studied the nitriding kinetics of high purity silicon powder after various polymer & solvent exposure and removal conditions. Surface chemistries, nitriding kinetics and resultant reaction gradients are compared to those of earlier work with pure silicon.

5. **A Study of the Microstructure of Reaction Bonded Silicon Nitride and Its Effect on Fracture Toughness**, L.M. Ewart, A. Lightfoot and J.S. Haggerty, presented at the 93rd Annual Meeting and Exposition of the American Ceramic Society, Cincinnati, OH, April 1991.

ABSTRACT

We have investigated the bulk material properties, microstructure and fracture mode of silane derived reaction bonded silicon nitride (RBSN). Despite similar processing histories fracture toughness values differ by a factor of 1.5 between batches. A characterization of the bulk properties including the use of X-ray diffraction, BET and bulk density measurements showed no significant differences. Detailed TEM and low voltage SEM studies revealed microstructural variations such as size and distribution differences in the porosity of the high and low toughness samples. While the total percent porosity remains relatively constant the percent of porosity greater than $0.1\ \mu\text{m}$ is up to 3 times greater in the low toughness samples. This results in clear changes in the intergranular crack path which were demonstrated by topographical analysis of the fracture surfaces.

THESES

1. **The Use of a Linear Regression Model and Statistical Significance to Adjust and Interpret Strength Measurements of Reaction Bonded Silicon Nitride**, F.M. Yee, B.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, June 1989.

ABSTRACT

Linear regression and statistical significance tests were selected to aid in the interpretation of strength data from the ball-on-ring biaxial flexural testing of silane-originating reaction bonded silicon nitride (RBSN). Linear regression was employed to obtain the best estimate of the actual fracture toughness of the RBSN groups. The Student t-test and F-test were selected to help discern from the fracture toughness values whether the populations they represented differed significantly. An analysis using these techniques was used to re-evaluate data from an oxidation effects and methanol removal effects on RBSN study. It was found that the two populations were statistically different in contradiction to an earlier evaluation.

2. **Mechanical Properties and Fractography Analysis of Particulate Silicon Carbide Reinforced Reaction Bonded Silicon Nitride Composites**, Hsien-Liang Ker, S.M. Thesis, Department of Materials Science and Engineering, Massachusetts Institute of Technology, June 1990.

ABSTRACT

Particulate SiC reinforced reaction bonded silicon nitride (SiC(p)/RBSN) composites were fabricated by nitriding high purity, silane-derived SiC and Si powder mixtures. The mechanical properties and microstructure of the composites were investigated and fractography analysis was used to study the crack-microstructure interactions in the composites. It was shown that in these composites the RBSN matrix retains its unique characteristic microstructure. The inherent porosities in this RBSN matrix were fine ($<0.4\ \mu\text{m}$) and uniformly distributed. The population of large processing-induced flaws in the composites were reduced and the flaw sizes were minimized with an average of 20 to $30\ \mu\text{m}$. Without further optimization, the 10 wt% SiC(p)/RBSN composite material has an average strength of 517 MPa, which is

superior to that of a commercially optimized product. However, contrary to what was expected, the fracture toughness of the composites were not improved as compared with that of the monolithic RBSN. The ultrafine SiC powders (average diameters = 0.04 to 0.05 μm) used in this study were found to form agglomerates, and it is speculated these SiC agglomerates is responsible for the decreased fracture toughnesses in the composites.

The toughening mechanisms in the composites were modelled to evaluate the effects of the microstructural features on the resulting fracture toughness of the composites. It is considered that crack deflection by small SiC agglomerates contributes to an increase in the critical strain energy release rate; on the other hand, large SiC agglomerates reduce the effective fracture surface area and cause an reduction in the Young's moduli of the composites. The result of the calculations to estimate the relative effects of these factors suggests that the toughening effect of the SiC agglomerates is very limited.

3. **Characterization of Toughness and Toughening Mechanisms in Particulate and Whisker Reinforced Reaction Bonded Silicon Nitride Matrix Composites**, Peter Zheng-Quan Cai, M.S. Thesis, Department of Mechanical Engineering, University of Massachusetts, December 1991.

ABSTRACT

Techniques for the measurement of toughness by indentation methods is first extended in a general way to the measurement of the fracture resistance, K_R , for materials that exhibit an R-Curve, by conducting both indentation as well as conventional fracture mechanics tests on a range of fully dense aluminas of different grain sizes. It is shown that suitable calibration factors can be obtained whereby correct absolute values of K_R can be obtained by coupling both post-indentation strength and indentation flaw size measurements. Next, the applicability of indentation techniques to a measurement of K_C and K_R in reaction bonded silicon nitride (RBSN) and RBSN composites containing a unique microporous and co-continuous pore and solid phase microstructure is investigated. It is found that the porous structure does not appear to result in any densification residual stresses when compared to that for fully dense ceramics. The magnitude of the indentation toughness compares well with toughness obtained by fractographic methods, an independent measure of toughness.

Finally, K_C , and K_R where applicable, is measured using indentation methods for a range of monolithic RBSNs, RBSN reinforced with SiC particulates of varying particle sizes and volume fractions, and one batch of SiC whisker reinforced RBSN, with a view to characterizing the role of SiC particulates and whiskers in strengthening and toughening of the RBSN matrix. Strengths were measured using the ball-on-ring method, and strength controlling flaws were examined in the SEM. No toughening was observed in the SiC whisker reinforced case, which appeared to be due to the particular morphology of the whiskers which prevented whisker pull-out and thereby enhanced whisker failure. Toughening was observed for SiC particulate reinforced RBSN, with the magnitude of toughening increasing with increasing SiC particle size and SiC volume fraction. Microstructural observations revealed crack deflection by the SiC particulates. Observed toughness enhancements were compared with the predicted toughness enhancements based on available models of particulate toughening. The experimental results were found to be qualitatively consistent with model predictions. No significant changes in the MOR strengths were observed due to SiC reinforcements except in the largest SiC particle (50 μm) case for which strengths were much smaller than for the base-line RBSN. In all

cases, strength controlling flaws were voids, except in the 50 μ m SiC particle reinforced RBSN, in which strength controlling flaws appeared to be large SiC agglomerations.

V. PARTICIPATING STAFF AND STUDENTS

STAFF

Massachusetts Institute of Technology

- Dr. John S. Haggerty (principal investigator)
- Professor Yet-Ming Chiang (co-investigator)
- Mrs. Annamarie Lightfoot (research scientist)
- Dr. Lynn Ewart (post doctoral research associate)
- Mr. David O'Connor (technician)
- Mr. Hsien-Liang (Charles) Ker (graduate student)
- Ms. Fung May Yee (undergraduate thesis student)
- Mr. Jeff Galvin (undergraduate UROP student)
- Mr. Andrew Heitner (undergraduate UROP student)
- Mr. Scott Jacobsmeyer (undergraduate UROP student)
- Mr. William Miller (undergraduate UROP student)
- Mr. Derek Mohar (undergraduate UROP student)
- Ms. Jane Song (undergraduate UROP student)
- Mr. Forrest Sprout (undergraduate UROP student)
- Mr. Hao Tung (undergraduate UROP student)

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- Professor Shanti Nair (principal investigator)
- Professor John Ritter (co-investigator)
- Dr. Sung Choi (post doctoral research associate)
- Mr. Zheng-Quan (Peter) Cai (graduate student)
- Mr. Jim Kohl (graduate student)
- Mr. John O'Leary (graduate student)

DEGREES AWARDED

- Ms. Fung May Yee
Bachelor of Mechanical Engineering
Massachusetts Institute of Technology
June 1989
- Mr. Hsien-Liang (Charles) Ker
Master of Science in Ceramics
Massachusetts Institute of Technology
June 1990
- Mr. Zheng-Quan (Peter) Cai
Master of Science in Mechanical Engineering
University of Massachusetts
December 1991

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